SHEMYAKIN, M.M ; MAYMIND, V.I.

Reaction mechanism of osazone formation. Dokl. AN SSSR 102 no.6: 1147-1150 Je'55. (MLRA 8:10)

1. Chlen-korrespondent Akademii nauk SSSR (for Shemyakin) 2. Institut biologicheskoy i meditsinskoy khimii Akademii meditsinskikh nauk SSSR
(Osazones) (Chemical reaction--Mechanism)

PAUSON, Peter L.; KHOKHLOV, A.S., kandidat khimicheskikh nauk [translator]; SHEMYAKIN, M.M., redaktor; ZAKHAL'YEVSKIY, V.A., redaktor; GERASIMOVA, Ye.S., tekhnicheskiy redaktor

[Chemistry of tropones and tropolones. Translated from the English] Khimiia troponov i tropolonov. Perevod s angliiskogo A.S.Khokhlova. Pod red. M.M.Shemiakina. Moskva, Izd-vo inostrannoi lit-ry, 1956. 204 p. (MLRA 9:7)

1. Chlen-korrespondent AN SSSR (for Shemyakin)
(Tropones) (Tropolones)

RODIONOV, V.M., akademik, redaktor [deceased]; KAZANSKIY, B.A., akademik, redaktor; KNUNYANETS, I.L., akademik, redaktor; SHEMYAKIN, M.M., redaktor; MEL'NIKOV, N.N., professor, redaktor; TAYTS, S.Z., redaktor; SHEMASTINA, Ye.V., redaktor; KORNEYEVA, V.I., tekhnicheskiy redaktor

[Reactions and methods of analysis of organic compounds] Reaktsii i metody issledovaniia organicheskikh soedinenii. Moskva, Gos. nauchno-tekhn. izd-vo khim. lit-ry. Vol.4. 1956. 319 p. (MLRA 9:7)

1. Chlen-korrespondent AN SSSR (for Shemyakin)
(Chemical reactions) (Isomers and isomerization)

SHEMYAKIN, M. M.

2

Advances of chemistry of antibiotics in recent years. A. S. Khokhlov and M. M. Shemyakin. *Khim. Nauka i Prom.* 1, 377–93(1956).—A review with 251 references of the progress made in detn. of structures of antibiotics including those of acyclic structures, tropolone derivs., aromatic derivs., chloromycetin, quinone derivs., *O*- and *N*-heterocyclic derivs., streptomycins, polypeptides, chromopeptides and several antibiotics whose structures are as yet incompletely established. The literature coverage includes 1955.
C. M. Kosolapoff

SHEMYAKIN, M. M.

According to the article, "Investigation in the Field of Sarcomyecin and Its Analogs. I. Synthesis of Dihydrocarbomyecin and Its Antipodes," by M. M. Shemyakin et. al., of the Institute of Biological and Medical Chemistry, Academy of Sciences USSR, Japanese chemists discovered sarcomyecin in 1954. The structure of this antibiotic was worked out, however, by a group of American scientists in the latter part of 1955. This compound is known to have antibacterial properties and is active against tumors. The American scientists also discovered that reduced sarcomyecin, i. e., dihydrocarbomyecin, has the same activity against tumors as the antibiotic itself.

Soviet scientists started seeking routes to the synthesis of sarcomyecin and its analogs toward the end of 1955. The present report constitutes the first publication of the results of this research. The authors studied and developed a new synthesis of the racemates of cyclopetanone-3-carboxylic and 2-methylcyclopnetanone-3-carboxylic acids. The latter of these acids was separated into optically active antipodes, one of which is identical to dihydrosarcomyecin. (Zhurnal Obshchey Khimii, Vol 27, No 3, Mar 57, pp 742-748) (U)

SUM. 1317

MAYMIND, V. I., [illegible] GOLUBEV, B., VIDOVINA, P. G., YERMOLAYEV, K. M., SHEMYAKIN, M. M.

Ref Zhur-Khimiya, No [illegible], 1957.

Investigation in the Field of Compounds, marked C14 and N15 IV. Synthesis Of Key Compounds.

Zh. obshch. Khimiyi, 1957, 26, No 7, 1962-1967.

Abstract : Described are methods of synthesis of phthalimide-N15 (I); of potassium salt of phthalimide-N15(II); HN1503 (III), HCl4N; salts of III-HN1502 and HC 14N. To 1.1 moles N15H3 (from 0.1 Mole N15H4NO3) are passed for 3 hours into a suspension of 0.015 mole of phtahlic acid in 400 cc water the solution is evaporated, the remainder is heated (200°) and sublimated (290-300°); then it is ground with water and neutralized with a 5% solution soda, yield is I, 98-99%. To a hot solution of 0.1 mole I is 350 cc anhydr., alcohol is added 50 cc 2N C2H5OK, yield is II, 98-99%, 0.15 mole N15H3 and 0.12, MNO2 is separated, the filtrate is evaporated to 250-300 cc, neutralized with 20% H2SO4, evaporated to dryness, and after adding 70 cc H2SO4, (d 1.5) III is distilled off. By neutralizeng III with alkalies the nitrates with a yield 82-84% are obtained. By the reduction of 0.01-0.05 mole KN 1502 (or NaN1503) by means of 0.015-0.075 g-atom Pb at 390° (for the preparation NaN1502-at 330°) KN1502: yield 91-93% is obtained. HCl4N is obtained with a yield 92-94% by a method described earlier (Maymind, V. I., Tokaryev, B. V. Shemyakin, M. M.

Dokl. AN SSSR, 1954, 81, 195), by heating (750-760°) BaCl·3 K and KN 3 in a current of N2 and subsequent neutralization with H2SO4. In order to obtain KCl·4N the vapors of Hcl·4N are passed through CaCl2 at 40° absorbed by anhydro. alcoholat -250, and precipitated wutg a solution of C2H5OK or spontaneously absorb Hcl·4N with solution of an alcoholate. The previous reports see RZhKhim, 1956, [illegible].

E-2

SHEMYAKIN M. M.

USSR/Organic Chemistry. Synthetic Organic Chemistry.

Abs Jour: Ref Zhur-Khimiya, No 6, 1957, 19284.

Author : Maymind V. I., Yermolayev Y. M., Shemyakin M.M.
Inst :
Title : Investigations in the Field of Compounds marked C14 and N15. V. Synthesis of -N15 amino acids.

Orig Pub: Zh. obshch. khimiyi, 1956, 26, No 8, 2313-2318.

Abstract: The synthesis of [illegible]-N15-aminoacids by condensation of phthalimide-N15-potassium (I) with the corresponding methyl esters of [illegible]-bromo-acids (MEB) and hydrolysis of the obtained phthaloyl derivatives (PD) with a mixture of CH_3COOH and HBr is described. By the action of CH_2N_2 on the corresponding bromoacids MEB are obtained: [illegible]-bromo-6-N-benzoylaminovaleric acid, m.p. (0-61° (purification -by washing with ether at -10°); [illegible]-bromo-[illegible]-N-phthaloylaminovaleric acid m.p. 61-62° (from ether);

Card : 1/4

[illegible]-N-benzoylaminocapronic acid, m.p. 43-44°

NESMEYANOV, A.N.; KHUNYANTS, I.L.; SHEMYAKIN, M.M.; BOGOSLOVSKIY, B.M.; SKURATOV, S.M.; KONKIN, A.A.; DERKVITSKAYA, V.A.; ROGOVIN, Z.

In memory of A.A. Strepikheev; obituary. Zhur.ob.khim.26 no.11:3224-3226 N '56. (MLRA 10:1)
(Strepikheev, Aleksandr Aleksandrovich, 1912-1955)

Shemyakin, M. M.

Chem

Synthesis of α-substituted α-amino acids and their derivatives. M. M. Shemyakin, E. S. Chaman, and L. I. Denisova. *Zhurnal Obshchei Khimii* 5.S.S.R. 106, 675-9(1956).—To 5 g. 2-phenyl-5-oxazolinone (I) in dry $(CH_2Cl)_2$ was added at 5° 2.5 g. Br_2 in $(CH_2Cl)_2$; the ppt. of I·HCl rapidly sepd. and the filtrate treated with dry ROH 1 hr. at room temp. gave the following: *BzNHCH(OMe)CO₂Me*, m. 86–7° (from Et_2O); *BzNHCH(OEt)CO₂Et*, m. 69–71° (from 70% EtOH); *BzNHCH(OPr)CO₂Pr*, m. 54–5° (from 70% EtOH); *BzNHCH(OC₅H₁₁)CO₂C₅H₁₁*, m. 52–3° (from MeOH); BzNHCH(OCHMe₂)CO₂CHMe₂, m. 80–1° (from 70% EtOH); *BzNHCH(OCMe₃)CO₂CMe₃* (II), m. 135–7° (from MeOH); *BzNHCH(OCH₂Ph)CO₂CH₂Ph*, m. 95–6° (from EtOH); *BzNHCH(OC₆H₁₁)CO₂C₆H₁₁*, m. 118–19° (from MeOH). The reaction with PhOH gave *BzNHCH(OH)CO₂Ph*, m. 159–60° (from MeOH). If after the bromination, the reaction with MeOH is run at 18–20° 5 hrs. the product from 4-methyl-2-phenyl-5-oxazolinone is *BzNHCMe(OMe)CO₂Me*, m. 114–15° (from MeOH-Et_2O). The procedure outlined above with I applied to abs. Me_3COH gave 23% II and 9% *BzNHCH(OCMe₃)CO₂H.H₂O* (III), m. 103–4° (from 70% EtOH), along with 39% *BzNHCH(OH)CO₂CMe₃*, m. 125–6° (from 70% MeOH); if use is made of Me_3COH contg. 3.6% moisture, there is obtained 48% III. III on further heating solidifies at 140° and remelts at 201° (decompn.). The brominated I, prepd. as above, treated at 0° with 0.27 g. H_2O and 6 ml. dioxane, followed by 3.4 g. $PhCH_2OH$ 1.5 hrs. at 20°, gave *BzNHCH(CO₂H)OCH₂Ph*, m. 123–5° (from 70% EtOH). Bromination of I followed by reaction with 1.7 g. $PhCH_2OH$ 1 hr. at 0° gave *BzNHCH(OH)CO₂CH₂Ph*, 31%, m. 125–6° (from 70% EtOH); if the mixt. is then treated with $PhNH_2$

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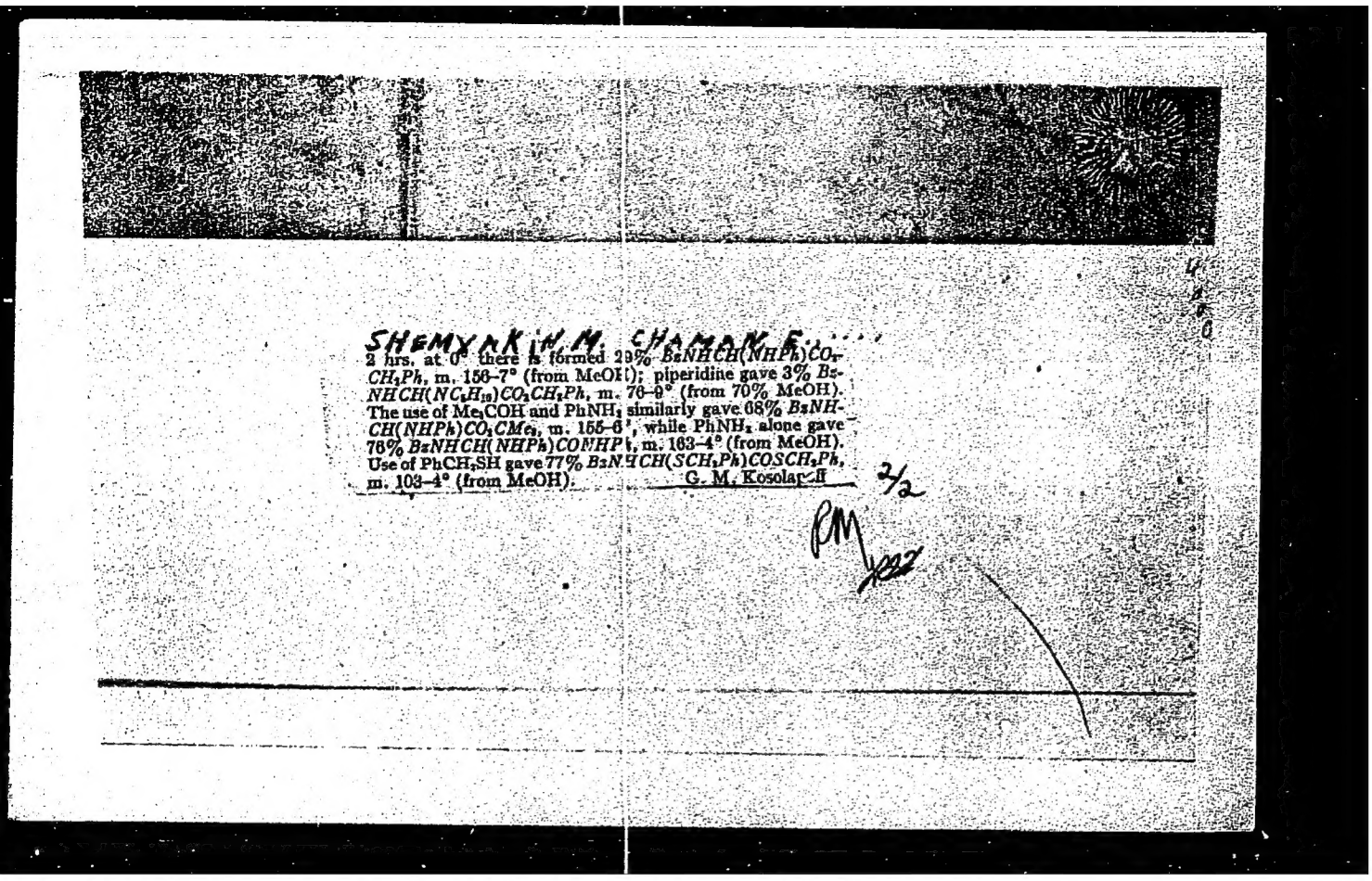

SHEMYAKIN M. CHAMOVE

2 hrs. at 0° there is formed 29% $BzNHCH(NHPh)CO_2CH_2Ph$, m. 156–7° (from MeOH); piperidine gave 3% $BzNHCH(NC_5H_{10})CO_2CH_2Ph$, m. 76–8° (from 70% MeOH). The use of Me_2COH and $PhNH_2$ similarly gave 68% $BzNHCH(NHPh)CO_2CMe_3$, m. 155–6°, while $PhNH_2$ alone gave 76% $BzNHCH(NHPh)CONHPh$, m. 163–4° (from MeOH). Use of $PhCH_2SH$ gave 77% $BzNHCH(SCH_2Ph)COSCH_2Ph$, m. 103–4° (from MeOH).

G. M. Kosolapoff

3/2

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SHEMYAKIN, M.M.; RAVDEL', G.A.; CHAMAN, Ye.S.

Synthesis of peptides containing an α-oxy-α-aminoacid residue. Dokl.AN SSSR 107 no.5:706-709 Ap '56. (MLRA 9:8)

1. Chlen-korrespondent AN SSSR (for Shemyakin); 2. Institut biologicheskoy i meditsinskoy khimii Akademii meditsinskikh nauk SSSR.
(Peptides)

USSR/ Physical Chemistry - Molecule. Chemical Bond. B-4

Abs Jour : Referat Zhur - Khimiya, No 3, 1957, 7233

fractional contribution of π-electron interaction energy to the total BH energy in percent (fourth number in parentheses), and the interatomic O...H distance calculated from standard bond dist. and the bond angles (fifth number in parentheses in A.U.) have been determined for the following compounds: the vapor of the monomethyl ether of ethylene glycol (I) at 120-122°(3665, 0, 0, 0, -); I in CCl_4 (II), in the ratio 1:400 (3605, 60, 0.96, 0, 1.80); phenol in II, 1:400 ratio (3605, 0, 0, 0, -); guaiacol in II, 1:400 (3530, 55, 0.90, 0, 2.20); oxyoctenol in II, 1:400 (3475, 147, 2.38, 59.7, 1.95); benzoin in II, 1:400 (3468, 147, 2.39, 60.0, 1.95); 2-hydroxy-1, 4-naphthoquinone in II, 1:400, 3398 (187, 3.07, 68.7, 2.25); 2-benzyl-3-hydroxy-1, 4-naphthoquinone in II, 1:600 (3395, 190, 3.11, 69.1, 2.25); 2-(β-naphthyl)-3-hydroxy-1, 4-naphthoquinone in II, 1:600 (3370, 215, 3.52, 72.7, 2.25); β-methyltropinone in II, 1:400 (3116, 504, 8.19, 88.2,

Card 2/4 - 30 -

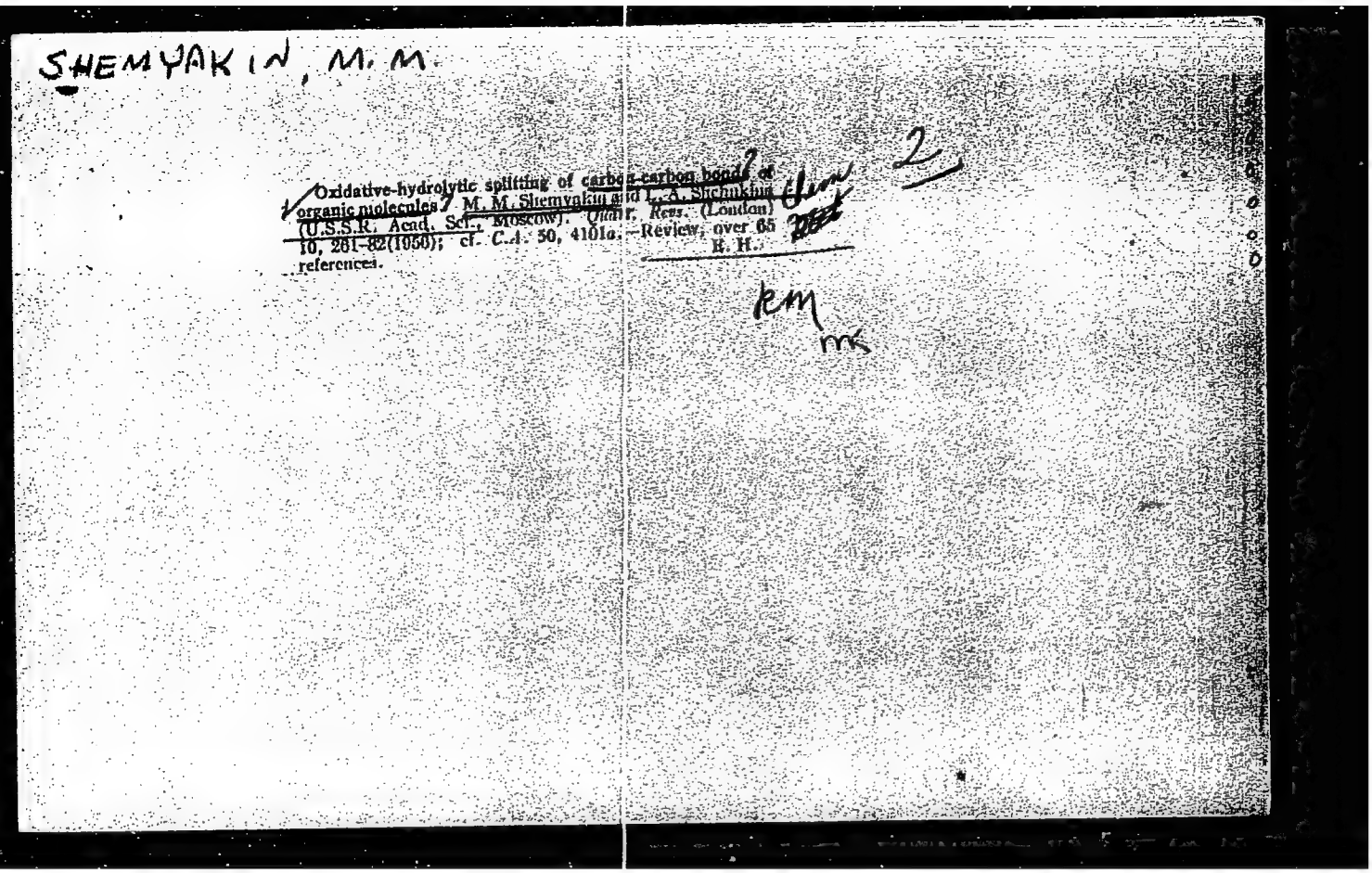
USSR/ Physical Chemistry - Molecule. Chemical Bond.

Abs Jour : Referat Zhur - Khimiya, No 3, 1957, 7233

2.25); vapor of the monomethyl ether of trimethylene glycol (III) at 160° (3650, 0, 0, 0, -); III in II, 1:400 (3580, 70, 1.12, 0, 1.65); o-methoxybenzyl alcohol (IV) vapor at 163-164° (3652, 0, 0, 0, -); IV in II 1:400 (3585, 67, 1.08, 0, 1.65); diacetone alcohol in II, 1:400 (3524, 94, 1.52, 26.2, 1.65); methyoxybenzoic acid in II, 1:400 (3357, 228, 3.74, 70.0, 1.65); salicylic acid vapor at 144° (3265, 320, 5.25, 78.7, 1.65); salol in II, 1:400 (3230, 355, 5.82, 80.7, 1.65); methyl salicylate in II, 1:400 (3205, 380, 6.23, 82.0, 1.65); acetylacetone in II, 1:400 (3050, 570, 9.26, 87.9, 1.65); monomethyl ether of 1, 8-dihydroxynaphthalene in II, 1:400 (3431, 189, 3.07, 63.5, 1.63); 9-hydroxy-1-methoxy-7-oxy-9-methyl-5,6,7,8-tetrahydroanthracene in II, 1:600 (3620, 0, 0, 0, -); 10-hydroxy-1-methoxy-7-oxy-9-methyl-5,6,7,8-tetrahydroanthracine in II, 1:400 (3423, 197, 3.20, 65.0, 1.63); 10-hydroxy-1-methoxy-9-methyl-

Card 3/4 - 31 -

"Synthese et Proprietes des Acides Amino et Substitutes," paper presented at the 16th International Congress of Pure and Applied Chemistry, Paris, 18-24 Jul 1957



SHEMYAKIN, M. M.

Oxidative-hydrolytic splitting of carbon-carbon bonds of organic molecules. M. M. Shemyakin and L. A. Shchukina (U.S.S.R. Acad. Sci., Moscow). *Quart. Revs.* (London) 10, 281–82(1950); cf. *C.A.* 50, 4101a. —Review, over 65 references. R. H.

SHEMYAKIN-M.M.

Chemistry of chloromycetin (levomycetin). VIII. Dependence of antimicrobic activity of chloromycetin on its structure and the mechanism of action of chloromycetin. M. M. Shemyakin, M. N. Kolosov, M. M. Levitov, K. I. Germanova, M. G. Karapetyan, Yu. B. Shvetsov, and E. M. Bamdas. *Zhur. Obshchei Khim.* 26, 773–82(1956); cf. *C.A.* 49, 16049*h*; 50, 3291*c*.—Biol. tests of several *N*-acyl derivs. of chloromycetin against *Staphylococcus aureus*, *Escherichia coli*, *Bacillus subtilis*, and *Vibrio fluorescens* were performed. The results indicate that the *p*-nitrophenyl group is important to the activity of the drug both through its electronic behavior and its polarizing action on the rest of the mol.; the geometric dimensions of this part of the mol. are not important in contrast to the import of geometric dimensions in the aminopropanediol portion of the mol. The NO_2 group can be shifted without loss of activity to other conjugated locations, and compds. with p-$O_2NC_6H_4$-N:N— or p-$O_2NC_6H_4CH$:N— linkages are highly active; compds. without the NO_2 group or those with it in unconjugated locations (p-$O_2NC_6H_4CONH$—) are inactive or weakly active. The biol. activity of chloromycetin analogs drops off in the series of the p-phenyl substituents: NO_2, CN, CO_2Me, Cl, SO_2Me, SO_2NH_2. Geometry and polarization in chloromycetin are discussed at length. New analogs were prepd. By heating 6 g. DL-*threo*-1(p-nitrophenyl)-2-amino-1,3-propanediol (I), 7.2 g. Me γ,γ,γ-trichlorocrotonate, and 4 ml. iso-AmOH to 110° 6 min., followed by treatment with

7

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Full translation available /m

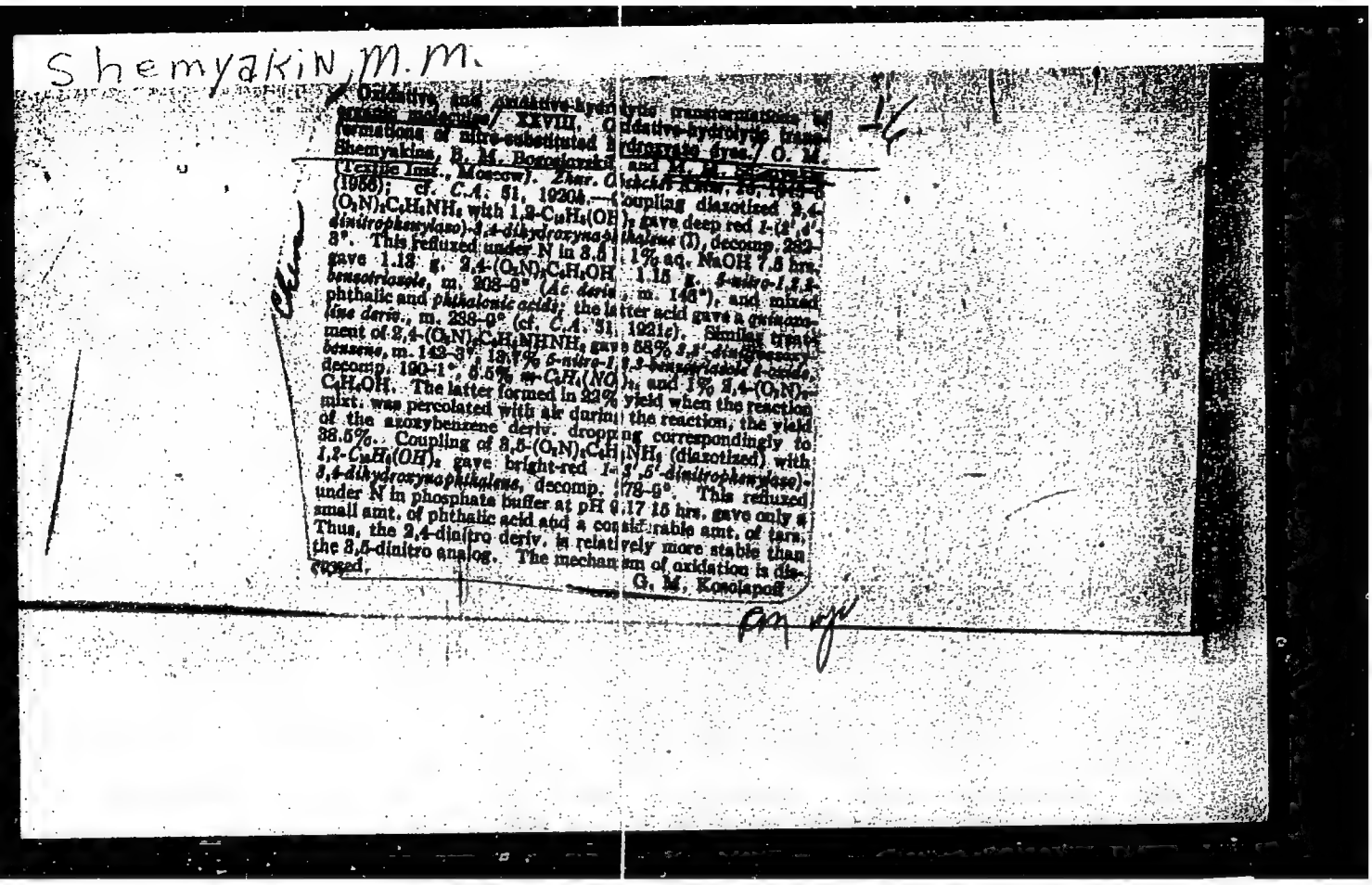
SHEMYAKIN, M.M. ...

EtOAc, gave 17% DL-*threo*-1(*p*-nitrophenyl)-2-(γ,γ,γ-trichlorocrotonylamino)-1,3-propanediol, m. 165–6° (from CH_3CH_2Cl). I (6 g.) in 350 ml. Et_2O and 190 ml. 0.5*N* KOH treated with 6.1 g. $CCl_3CH_2CH_2COCl$ (b_{10} 97°) 0.5 hr. gave 87% DL-*threo*-1(*p*-nitrophenyl)-2-(γ,γ,γ-trichlorobutyrylamino)-1,3-propanediol, m. 116–17° (from $(CH_2Cl)_2$). D- or L-form of I (9 g.) similarly treated with $CHCl_2CH:CHCOCl$ (b_{15} 79–81°, $n^{19}D$ 1.5155) gave 70–5% D-*threo*-1(*p*-nitrophenyl)-2-(γ,γ,γ-dichlorocrotonylamino)-1,3-propanediol, m. 84–5° (from EtOAc and $(CH_2Cl)_2$), $[\alpha]^{19}D$ −70.8° (Me_2CO); L-*threo analog*, m. 84–5°, $[\alpha]^{19}D$ 67.6° (Me_2CO); DL-*analog*, prepd. by mixing the 2 isomers, m. 144–5°. I (6 g.) in 300 ml. dry dioxane was treated at 12–15° with 2.45 g. $CCl_2:CHCH_2COCl$ over 0.5 hr.; after 0.5-hr. shaking the mixture was filtered and concd. *in vacuo*, treated with EtOAc, washed with dil. H_2SO_4 and 20% NaCl, and evapd., yielding 88% DL-*threo*-1(*p*-nitrophenyl)-2-(γ,γ-dichlorovinylacetamido)-1,3-propanediol (II) *hydrate* (from heptane and $(CH_2Cl)_2$ or EtOAc-$ClCH_2CH_2Cl$), m. 72–3°; the water of hydration is lost at 100° *in vacuo*. This (0.2 g.) in dry dioxane treated with 2 drops dry Et_3N and kept 45 hrs. gave 90% DL-*threo*-1-(*p*-nitrophenyl)-2-(γ,γ-dichlorocrotonylamino)-1,3-propanediol, m. 144–5°, identical with the above described. Refluxing II with 20% HCl 2 hrs. gave 87% $CCl_2:CHCH_2CO_2H$ and 91% I. G. M. Kosolapoff

2/2

SHCHUKINA, L.A.; SHEMYAKIN, M.M.

Oxidative and oxidative-hydrolytic transformations of organic molecules. Part 27: Tautomeric transformations and properties of hydroxy- and chloroketocarboxylic acids. Zhur.ob.khim. 26 no.6: 1708-1713 Je '56. (MIRA 11:1)
(Acids, Organic) (Tautomerism)



Shemyakin, M. M.

Oxidative and oxidative-hydrolytic transformations of aromatic compounds. XXVIII. Oxidative-hydrolytic transformations of nitro-substituted 1-hydrazinonaphthalenes. O. M. Shemyakina, B. M. Porozjanskii and [illegible] (Textile Inst., Moscow). *Zhur. Obshchei Khim.* 16, 1929-36 (1946); cf. *C.A.* 41, 1920h.—(O$_2$N)$_2$C$_6$H$_3$NH$_2$ with 1,2-C$_{10}$H$_6$(OH)$_2$ gave deep red *1-(2',4'-dinitrophenylazo)-2,4-dihydroxynaphthalene* (I), decomp. 282-3°. This refluxed under N in 3.5% aq. NaOH 7.5 hrs. gave 1.15 g. 2,4-(O$_2$N)$_2$C$_6$H$_3$OH, m. 142°), and mixed *benzotriazole*, m. 208-9° (*Ac deriv.*, m. 148°), and mixed phthalic and *phthalonic acids*; the latter acid gave a *quinone* deriv., m. 238-9° (cf. *C.A.* 31, 1921e). Similar treatment of 2,4-(O$_2$N)$_2$C$_6$H$_3$NHNH$_2$ gave 58% *2,4'-dinitroazobenzene*, m. 142-3°, 13.7% *5-nitro-1,2,3-benzotriazole-4-oxide*, decomp. 190-1°, 0.5% *m*-C$_6$H$_4$(NO$_2$)$_2$, and 1% 2,4-(O$_2$N)$_2$C$_6$H$_3$OH. The latter formed in 22% yield when the reaction mixt. was percolated with air during the reaction, the yield of the azoxybenzene deriv. dropping correspondingly to 38.5%. Coupling of 3,5-(O$_2$N)$_2$C$_6$H$_3$NH$_2$ (diazotized) with 1,2-C$_{10}$H$_6$(OH)$_2$ gave bright-red *1-(3',5'-dinitrophenylazo)-3,4-dihydroxynaphthalene*, decomp. 278-9°. This refluxed under N in phosphate buffer at pH 9.17 15 hrs. gave only a small amt. of phthalic acid and a considerable amt. of tars. Thus, the 2,4-dinitro deriv. is relatively more stable than the 3,5-dinitro analog. The mechanism of oxidation is discussed.

G. M. Kosolapoff

SHEMYAKIN, M.M.; SHCHUKINA, L.A.

Theory of oxidative and hydrolytic conversions of organic molecules [with summary in English]. Biokhimiia 22 no.1/2:214-225 Ja-F '57. (MLRA 10:7)

1. Institut biologicheskoy i meiitsinskoy khimii Akademii meditsinskikh nauk SSSR, Moskva.
(CHEMISTRY, ORGANIC,
theory of oxidative-hydrolytic conversion of organic molecules, review (Rus))

Shemyakin, M.M.

7
4E4j
4E3d
4E2cGj
2-may
1-RmL

Compounds labeled with carbon-14 and nitrogen-15. VI. New method of study of dual reactivity and tautomerism. VII. Study of the triazene (diazoamine) system. M. M. Shemyakin, V. I. Maimind, and E. Comes. *Zhur. Obshchei Khim.* 27, 1842–9(1957). cf. *C.A.* 51, 4944h.—Treatment of 7.35 g. N^{15}-phthalimide in 20 ml. H_2O with 30 ml. 30% NaOH at 30° followed by 2.8 ml. NaOBr from 2.8 ml. Br, 9 g. NaOH, and 25 ml. H_2O precooled to 0°, gradual cooling to 0° and acidification with HCl to pH 4, and addition of 10–15 ml. AcOH gave 80–5% N^{15}-anthranilic acid; this on pyrolysis gave $PhN^{15}H_2$. Diazotization of unlabeled $PhNH_2$ in aq. HCl, addn. of acetate buffer of pH 6.38, filtration if necessary, and addn. of $PhN^{15}H_2$ in MeOH gave 90% diazoaminobenzene, m. 100°, in which the label is on one of the end N atoms. Similar reaction of $PhNH_2$ and $NaN^{15}O_2$ gave diazoaminobenzene labeled at the middle N atom. Isomerization of these in AcOH (Rosenhauer and Unger, *C.A.* 22, 1761) gave aminoazobenzene, which was diazotized and decompd. in the presence of hydroquinone, or was thermally decompd. at 150°. The examn. of isotope distribution of N in the products shows that PhN:NNHPh is a nearly equimolar isomer mixt. with PhNNH:NPh and that the triazene system is highly mobile. The dual reactivity of the compd. is not connected with transfer of the reactive center from one N atom to another during reactions. Acylation with $Ph_2C{:}CO$ gave the *N*-diphenylacetyl deriv., decomp. 143°, whose decompn. indicated the equalization of isotope compn. of N on the terminals atoms of the triazene.

G. M. Kosolapoff

Phys 1

SHEMYAKIN, M. M.

Distr: 4E4j/4E3d/4E2c(j)

V Mechanism of azoxy coupling reaction. M. M. Shemyakin, V. I. Maimind, and B. K. Vaichunaite. *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1957, 1260–2.—To 0.5 g. PhNHOH in 10 ml. EtOH was added at 10° 0.5 g. PhN^uO in EtOH, the mixt. treated with 0.8 ml. 7% alc. KOH and, after 2 min., neutralized with H_2SO_4, yielding 92% azoxybenzene/corr. with N^u. This was brominated (cf. Angeli and Valori, *C.A.* 6, 1137) to 4-bromoazoxybenzene-N^u, m. 73°, which heated with Sn-HCl and the crude product treated with Ac_2O yielded 90% *p*-BrC_6H_4NH-Ac and 38% PhNHAc. The N^u content in atom percent in these products was: 37.2 in PhNO, 19.1 in PhNHAc, and 18.2 in *p*-BrC_6H_4NHAc. Thus N^u excess was distributed equally among the cleavage products, indicating the formation of an intermediate compd. with equiv. locations of the N atoms, such as $(PhN^uOH)_2$. G. M. K.

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SHEMYAKIN, M.M.; RAKHEL', G.A.; CHAMAN, Ye.S.; SHVETSOV, Yu.B.; VINOGRADOVA, Ye.I.

Synthesis of racemic sarkomycin. Izv. AN SSSR. Otd. khim. nauk no.8:1007 Ag '57. (MIRA 11:2)

1. Institut biologicheskoy i meditsinskoy khimii Akademii meditsinskikh nauk SSSR.

(Sarkomycin)

TERENT'YEV, A.P.; YANOVSKAYA, L.A.; RUKHADZE, Ye.G., redaktor; RODIONOV, V.M., akademik, redaktor [deaceased]; KAZANSKIY, B.A., akademik, redaktor; KNUNYANTS, I.L., akademik, redaktor; SHEMYAKIN, M.M., redaktor; NEL' NIKOV, N.N., prof, redaktor; LUR'YE, M.S., tekhnicheskiy redaktor.

[Polarographic analysis in organic chemistry] Poliarograficheskii method v organicheskoi khimii. Moskva, Gos. nauchno - tekhn. izd-vo khim. lit-ry, 1957. 388 p. (Reaktsii i metody issledovaniia organicheskikh soedinenii, vol.5) (MIRA 10:10)

1.Chlen-korrespondent AN SSSR (for Shemyakin).
(Polarography) (Chemistry, Organic)

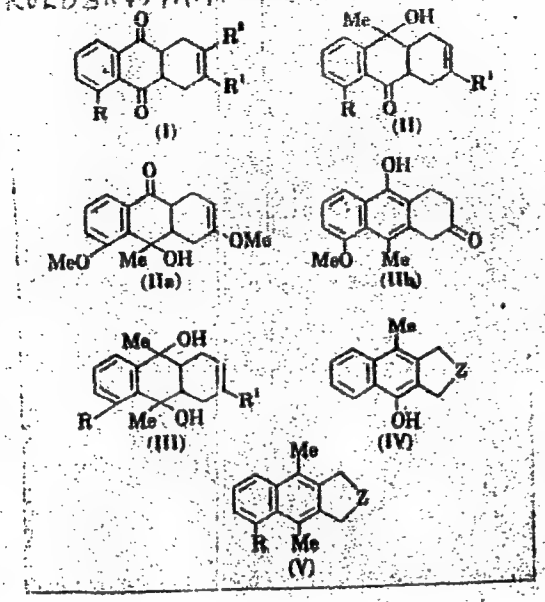
Shemyakin, M.M.

Initial stages of synthesis of tetracyclines. M. M. Shemyakin, M. N. Kolosov, M. G. Ter-Arapetyan, and E. S. Chaman. *Doklady Akad. Nauk S.S.S.R.* 112, 669–72(1957).—Initial steps of the syntheses of the tetracycline group of antibiotics are reported. Condensation of 1,4-naphthoquinones with butadiene and its derivs. at 100° gave the following (I) (R, R^1, R^2 given): *H, MeO, H*, 23%, m. 143–4°; *MeO, H, H*, 91%, m. 93–4° (λ 229 and 330 mμ); *AcO, H, H*, 91%, m. 113.5–14.5° and 135.5–6.5°. The condensation of 5-methoxynaphthoquinone with CH_2:CHC(OMe):CH_2 was run in C_6H_6 under CO_2 12 hrs. at 100° yielding 94% mixed isomers which gave 55% I (*MeO, H, MeO, H*), m. 144–5° (λ 227 and 338 mμ), and I (*MeO, H, MeO*), 15%, m. 141–3° (λ 227, 338 mμ), the structures of which were proved by oxidation to the dimethoxyanthraquinones, and hydrolysis to the *dihydroxyanthraquinones*, identified as the *diOAc derivs.*, m. 197–8°, and 204–5°, resp. I in C_6H_6 gradually treated with strong cooling with MeMgI (not over 25% excess) yielded II (R, R^1 given): *H, H*, 70%, m. 135–7° (λ 248 and 291 mμ); *MeO, H*, 12%, m. 194–6° (λ 250 and 317 mμ). I (*MeO, MeO, H*) gave 2 products: II (*MeO, MeO*), 12%, m. 191–3°, and IIa, 19%, m. 137.5–8.5°. The structures were proved by conversion to 1,8- and 1,10-hydroxymethoxyhydroanthracenes whose infrared spectra showed typical chelation of HO with MeO groups. Use of excess MeMgI and reversal of the order of addn. gives III (R and R^1 given): *H, H*, m. 160–7° (λ 238, 260, 285, and 297 mμ); *H, MeO*, 40%, m. 171–2°; *MeO, H*, 49%, m. 140–40° (λ 272 and 279 mμ). The ketols and the glycols were stable in air in contrast to the I;

Kolosov, M.N.; Karapetyan, M.G.; Chaman, E.S.

this indicates a trans structure of the former compds. owing to epimerization of 1 of the asym. centers. The C-10-asym. center can be examd. on the basis of the postulates of Cram and Elhafez (*C.A.* 48, 2046*e*), which lead to the Me group being cis in respect to the H on C-10a. Thus, II correspond geometrically to the natural tetracycline antibiotics. This is confirmed by acidic treatment of III which leads to their dehydration. Heating with aq. alc. HCl 0.5 hr. at 60° leads to dehydration to the following IV (*R* and *Z* given): H, CH:CH, 83%, m. 117–19° [*acetate*, m. 153–6°; *Me ether*, m. 97–9° (λ 230, 288, 297 mμ)]; *MeO*, *CH:CH*, 96%, m. 115–16° (λ 241, 311, 334 and 339 mμ) [*dihydro deriv.*, m. 107.5–8° (λ 237, 312, 324, and 339 mμ)]. III (*R* = *MeO*, *R'* = *H*) gave 90% V (*R* = *MeO*, *Z* = *CH:CH*), m. 115–

Kolosov, M.N., [illegible] M.G., & Chaman, E.S.



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3/4

Kolosov, M.N.; Karapetyan, M.G.; Chaman, E.S.

15.5° (λ 241, 296, 306, 319, and 333 mμ). The keto alcs. and the glycols, which are really enol derivs., are attacked by HCl under the above conditions yielding the corresponding ketones of the tetrahydroanthracene group. Thus II ($R = R^1 = MeO$) gave IV ($R = MeO, Z = CH_2CO$), m. 136–7°, while IIa gave IIb, m. 170–3°. III ($R = H$, $R^1 = MeO$) gave 94% IV ($R = H, Z = CH_2CO$), m. 120–1°. If the substance, however, is shaken in Et_2O with 1–2% HCl at 20° only the MeO group of ring C is attacked. Thus, III ($R = H$, $R^1 = MeO$) give 53% *2-oxo-9,10-dihydroxy-9,10-dimethyl-1,2,3,4,4a,9,9a,10-octahydroanthracene*, m. 135–6°.

G. M. Kosolapoff

4/4

The Tautomerism of Arylazotropolones. 20-3-29/59

in position 3.On this occasion they change into corresponding 5-arylazo-4-carboxylmethyl tropolones(VII);this reaction does not take place in the case of the initial tropolon(IIIg),in the case of the tautomeric models V g-V e,however,absolutely natural,where the separatable carboxyl group is in a ß-position with respect to one of the carbonyl groups.Finally it was found that on the occasion of the transformation of the arylazotropolones IVg-IVe into acids(VII) and also directly from the latter,slightly neutral compounds(VIII) are formed as a consequence of closing the heterocycle of the tropochinonhydrazon forms of the arylazotropolones.The knowledge about the tropochinonhydrazon tautomerism of the arylazotropolones I⇄II which were obtained by chemical investigation could be confirmed spectroscopically.The capacity of the arylazotropolones for the above discussed tautomerism was recently noticed by Nozoe who also observed the formation of the chinoxalin-derivates with o-phenylendiamine.In the experimental part the usual data concerning the production methods and the constants of the substances in question are given. There is 1 table and 1 Slavic reference.

Card 2/2

ASSOCIATION Institute for Biological and Medical Chemistry of the Academy of Medical Sciences of the USSR and of the Moscow Textile Institute. (Institut biologicheskoy i meditsinskoy khimii Akademii meditsinskikh nauk SSSR,Moskovskiy tekstil'nyy institut).

SUBMITTED June 17, 1957
AVAILABLE Library of Congress

RODIONOV, Vladimir Mikhaylovich, akademik [deceased]; ZVORYKINA, V.K., sostavitel'; KISELEVA, V.V., sostavitel'; FEDOROVA, A.M., [translator]; KNUNYANTS, I.L., akademik, otv.red.; SHEMYAKIN, M.M., akademik, otv.red.; SHVETSOV, Yu.B., red.izd.; POLENOVA, T.P., tekhn.red.

[Selected works] Izbrannye trudy. Moskva, Izd-vo Akad. nauk SSSR, 1958. 792 p. (MIRA 12:2)
(Chemistry, Organic)

SHEMYAKIN, M. M. (Moscow, USSR)

"Einige Wege zur Synthese von Tetracyclinen"

report submitted for IV Intl. Cong. of Biochemistry, Vienna, 1-6 Sept 1958.

SOV/62-58-6-34/37

AUTHORS: Shemyakin, M. M., Kolosov, M. N., Arbuzov, Yu. A., Onopriyenko, V. V., Shatenshteyn, G. A.

TITLE: The Course Taken by the Synthesis of Ring A of Tetracyclic Compounds (Put' sinteza kol'tsa A tetratsiklinov)

PERIODICAL: Izvestiya Akademii nauk SSSR, Otdeleniye khimicheskikh nauk, 1958, Nr 6, pp. 794-795 (USSR)

ABSTRACT: Already in 1957 the authors of this report described the synthesis of tricyclic compounds in which 2 rings, with respect to their structure, resemble rings D and C of tetracyclinic compounds. The third ring, which corresponds to ring B, contains a binary compound or a potential carbonyl group. At present the authors are studying the possibility of synthetizing ring A and describe this synthesis. The group CHX . CO_2 is introduced into the initial ketone, ketone ester is ethylated, ethynyl carbinol (formula III) Y=C≡CH is hydrated in the neutral medium and oxy-ketoester (formula II; Y=Ac) is cyclized into an oxy-diketone (formula III; Z=H). (Formula III; Z=CONHR). The scheme has the following form:

Card 1/3

The Course Taken by the Synthesis of Ring A of Tetracyclic Compounds

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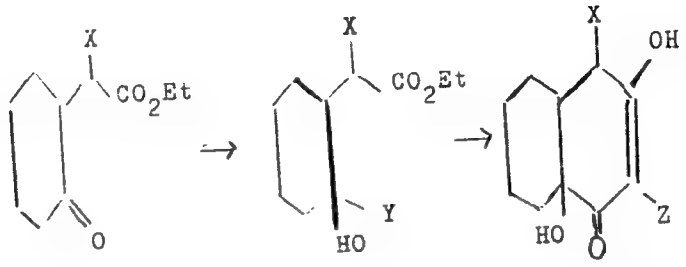


(I) (II) (III)

There are 2 references, 1 of which is Soviet.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR i Institut biologicheskoy i meditsinskoy khimii Akademii meditsinskikh nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy, AS USSR and Institute of Biological and Medico-Chemistry of the Academy of Medical Sciences of the USSR.)

SOV/62-58-9-22/24

AUTHORS: Shigorin, D. N., Shemyakin, M. L., Kolosov, M. N.

TITLE: Intermolecular Interactions Between Acetylene and Its Derivatives (Mezhmolekulyarnyye vzaimodeystviya u atsetilena i yego proizvodnykh)

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1958, Nr 9, pp 1133 - 1134 (USSR)

ABSTRACT: Considering the peculiarities of the chemical structure of acetylene and its derivatives the authors considered it possible that these compounds might be able to form complexes with one another and with solvents. These complexes could result from the hydrogen bridge bonds R-C ≡ C-H.X (X= O<, O = C<, N<, — C ≡ C, and so forth). The study of the infrared absorption spectra showed frequency changes in the ≡ C-H and — C ≡ C - groups of acetylene and its derivatives in dissolving in acetone, ether, pyridine, and dioxane, in sublimating from the crystalline to the vapor state and in solutions of CCl_4. This probably means that the acetylene molecule forms complexes with the molecules

Card 1/3

Intermolecular Interactions Between Acetylene and Its Derivatives

SOV/62-[illegible]-[illegible]/[illegible]

of the solvent by forming hydrogen bonds. The union of the acetylene molecules and the homologs and derivatives of acetylene is apparently possible because of the electron shift in the ≡C - H and -C≡C- bonds (which also belong to many other molecules). For this reason intermolecular electron orbitals are hypothesized. The authors discovered a new phenomenon in intermolecular interaction. It was shown experimentally that the formation of hydrogen bridge bonds and π complexes among the molecules of acetylene and its derivatives is possible. It was demonstrated that the hydrogen of the ≡ C-H group exchanges with deuterium in the dissolution of R - C≡CH compounds in CH_3OD or C_2H_5OD. For R-C≡CD in CCl_4 the following frequencies were found:

$\nu(\equiv C\text{-}D) = 2600\ cm^{-1}$; $\nu(-C\equiv C-) = 1957\ cm^{-1}$. There is 1 table.

Card 2/3

Intermolecular Between Acetylene and Its SOV/62-58-9-22/24
Derivatives

ASSOCIATION: Fiziko-khimicheskiy institut im.L.Ya.Karpova (Physical-Chemical Institute imeni L.Ya.Karpov) Institut biologicheskoy i meditsinskoy khimii Akademii meditsinskikh nauk SSSR (Institute of Biological and Medical Chemistry of the Academy of Medical Sciences of the USSR)

SUBMITTED: June 24, 1958

Card 3/3

79-28-4-29/60

AUTHORS: Shemyakin, M. M., Maymind, V. I., Tokarev, B. V., Karpov, V.I.

TITLE: Investigation of Stephen's (Stefen) Reaction (Izucheniye reaktsii Stefena) (Report VII From the Series "Investigations in the Field of Compounds Marked by C^{14} and N^{15}". Previous Report See Reference 1)

PERIODICAL: Zhurnal Obshchey Khimii, 1958, Vol.28, Nr 4, pp. 978-983 (USSR)

ABSTRACT: In the investigation of the synthesis of amino acids marked by radioactive carbon the authors had to apply Stephen's reaction for the production of aliphatic aldehydes from corresponding nitriles. As so far Stephen's reaction in this case provided not very satisfactory results, the authors were forced to settle the best conditions of its development at the example of the production of one of the aldehydes of the aliphatic series (iso-valeric anhydride). Later these conditions were also extended to the synthesis of other aldehydes - acetaldehyde and phenylacetaldehyde. The following was ascertained as a result of the investigations: 1) The salt of the aldimine and of the hexachlor stannic acid which develops immediately

Card 1/3

79-28-4-29/60

Investigation of Steph[illegible] (Stefen) Reac[illegible] [illegible] From the Series "Investigations in the Field of Compounds Marked by C[illegible] Previous Report See Reference 1)

during the reaction can be dissolved in the reaction medium up to a certain degree. The salt of the phenylacetaldimine entirely deposits as sediment, whereas the salt of the acetaldimine partly remains in solution, and the salt of the iso-valeric aldimine dissolves entirely. For this reason in Stephen's reaction in every new case not only the sediment but also the residue after the separation of the solvent must be investigated. 2) The best reaction temperature is in the range of 15 to 25°C (Table 1). 3) The optimum duration of the reduction reaction is 7 days (Table 2). 4) The best quantity of stannic chloride in the production of the iso-valeric aldehyde is 7 moles to 1 mole of nitryl (Table 3). 5) Presence of water in the reaction medium effects a diminution in the yield of aldehydes (Table 4). As a result of the investigations it has been ascertained that the yield of iso-valeric aldehyde under the best conditions is 61 - 64 %, of acetaldehyde 64 - 67 % and of phenylacetaldehyde 55 - 60 %. It has been shown that the transformation reaction of nitryls into imino ethers competes with the reduction

Card 2/3

79-28-4-29/60

Investigation of Steffen's (Stefen) Reaction. (Report VII From the Series "Investigations in the Field of Compounds Marked by C^{14} and N^{15}". Previous Report See Reference 1)

reaction of nitryls to aldimines. The transformation reaction takes place under the influence of alcohol developed in consequence of the decomposition of ethyl ether by hydrogen chloride. At higher temperatures this process can entirely prevent the reduction of nitryl. Starting from $KC^{14}N$ the reduction of benzilcyanide to phenylacetaldehyde after Steffen was used for the synthesis of the phenylalanine-2-C^{14}. There are 4 tables and 26 references, 4 of which are Soviet.

ASSOCIATION: Institut biologicheskoy i meditsinskoy khimii Akademii meditsinskikh nauk SSSR (Institute for Biological and Medical Chemistry of the Academy of Medical Sciences USSR)

SUBMITTED: March 18, 1957

Card 2/2

SOV/79-28-6-61/63

AUTHORS: Shemyakin, M. M., Maymind, V. I. Vaychunayte, B. K.

TITLE: Letters to the Editor (Pis'ma v redaktsiyu) Investigation of the Wallach Regrouping and Its Related Reactions (Izucheniye peregruppirovki Vallakha i rodstvennykh yey reaktsiy)

PERIODICAL: Zhurnal obshchey khimii, 1958, Vol. 28, Nr 6, pp. 1708 - 1709 (USSR)

ABSTRACT: Lately the authors explained the reaction mechanism of the azoxy binding by means of N^{15} (Ref 1) and found that this process takes place through the stage of formation of the intermediate dioxy compounds. At present they use N^{15} for the investigation of various isomerizations of azoxy compounds - of the Wallach regrouping and of its related reactions. For this purpose the $C_6H_5N^{14}(O)=N^{15}C_6H_5$ (Refs 2,3) was synthetized from $C_6H_5N^{15}H_2$ and $o\text{-}O_2N^{14}C_6H_4CHO$; the product was then subjected to a regrouping into the o- and p- oxyazobenzenes on different conditions. The isotopic composition of the nitrogen in azoxybenzene was determined by bromination and subsequent reduction cleavage (Ref 1),

Card 1/3

and in the oxyazobenzenes by reduction with tin in concentrated hydrochloric acid at 85-90°. It was found that in the presence of chlorosulfonic acid (Ref 4) the regrouping of azoxybenzene into the p-oxyazobenzene is accompanied by a complete balance of the isotopic composition of either nitrogen. On the action of 83% sulfuric acid on azoxybenzene the same results were obtained, which does not agree with the statements in publications. From the experiments carried out for this purpose follows that the conversion of the azoxybenzone into the p-oxyazobenzene takes place in two different ways: in the one way - the main way mentioned in scheme 1 - this regrouping takes place through the stage of oxide formation, and in the other way - the secondary way mentioned in scheme 2 - it takes place without touching this stage. The regrouping under the influence of ultraviolet light was only little accompanied by the balance of the isotopic composition of the nitrogen of the o-oxyazobenzene (Scheme 3). There are 5 references, 2 of which are Soviet.

Letters to the Editor. Investigation of the Wallach SOV/ 79-28-6-61/63
Regrouping and Its Related Reactions

ASSOCIATION: Institut biologicheskoy i meditsinskoy khimii Akademii meditsinskikh nauk SSSR (Institute of Biological and Medical Chemistry, Academy of Medical Sciences USSR)

SUBMITTED: February 24, 1958

1. Azoxybenzene--Synthesis

Card 3/3

SOV/79-28-8-15/66

AUTHOR: Shemyakin, M. M., Kolosov, M. N., Karapetyan, M. G., Podionov, V. Ya.

TITLE: Investigations on Sarcomicin and Its Analogs (Issledovaniya v oblasti sarkomitsina i yego analogov) II. Synthesis of the Sarcomicin Isomer (II. Sintez izomera sarkomitsina)

PERIODICAL: Zhurnal obshchey khimii, 1958, Vol. 28, Nr 8, pp. 2068-2074 (USSR)

ABSTRACT: In connection with a previous publication on sarcomicin (Ref 1) the authors worked on synthesizing this antibiotic (Formula I) and its ethyl ester isomer (II), which differs from sarcomicin in the positions of its methylene groups. Although sarcomicin has a simple structure its synthesis is especially difficult because it is easily oxidized and has a tendency to polymerize and to form isomers. Therefore, an energetic reaction cannot be carried out, and only mild reagents and lowered reaction temperatures can be used. Since the characteristic β-methylene-γ-keto-acid group in sarcomicin cannot stand strong treatment the splitting of quarternary ammonium salts of the type

Card 1/3

Investigations on Sarcomicin and Its Analogs. II. Synthesis of the Sarcomicin Isomer

SOV/79-28-6-15/66

$-COCH(CH_2\overset{+}{N}R_3)-$ seemed to be a promising synthetic method. One can synthesize in various ways the compounds of type (III) necessary for producing sarcomicin. The simplest way to synthesize these compounds was to use the easily obtainable cyclopentanone-3-carbonic acid (IV), by introducing the dialkyl aminomethyl group into the 2 position by the Mannich reaction and then halogenalkylating the resulting tertiary amine. The synthesis of the isomer of the antibiotic sarcomicin (which is used against malignant tumors) was accomplished in this way. The starting material was cyclopentenone-3-carbonic acid. This compound was condensed with formaldehyde and piperidine. The next steps were esterification and iodomethylation, and the end-product was then converted to the corresponding quarternary ammonium salt. The splitting of the salt yielded the ester of the iso-sarcomicin. There are 10 references, 2 of which are Soviet.

ASSOCIATION: Institut biologicheskoy i meditsinskoy khimii Akademii meditsinskikh nauk SSSR (Institute of Biological and Medical Chemistry of the Academy of Medical Sciences, USSR)

Card 2/3

PHASE I BOOK EXPLOITATION SOV/3494

Reaktsii i metody issledovaniya organicheskikh soyedineniy, Kn. 8 (Reactions and Research Methods of Organic Compounds, Bk. 8) Moscow, Goskhimizdat, 1959. 446 p. Errata slip inserted. 4,200 copies printed.

Eds (Title page): V.M. Rodionov, Academician (Deceased), B.A. Kazanskiy, Academician, I.L. Knunyants, Academician, M.M. Shemyakin, Academician, and N.N. Mel'nikov, Professor; Ed. (Inside book): V.P. Yevdakov; Tech. Ed.: V.F. Zazul'skaya.

PURPOSE: This book is intended for laboratory personnel at industrial plants, for instructors and students at higher educational establishments, and particularly for scientists and researchers working at the numerous research institutes in the Soviet Union.

COVERAGE: This is the eighth volume in a series "Reactions and Research Methods of Organic Compounds." This series does not duplicate the one published in English under the title "Organic Reactions" and appearing in Russian translation; however, some material, of particular interest, is included in this publication. The present series is primarily devoted to reviewing the works of Soviet chemists. The eighth volume of this series deals with thiocyanation

Card 1/6

5(3)

AUTHORS: Shemyakin, M. M., Denisova, L. I., Chaman, Ye. S. SOV/62-59-4-19/42

TITLE: Investigations in the Field of the α-Substituted α-amino Acids (Issledovaniya v oblasti α-zameshchennykh α-aminokislot). Communication 5. Methods of Preparing Substituted α,α-Diamino-carboxylic Acids (Soobshcheniye 5. Sposoby polucheniya zame-shchennykh α,α-diaminokarbonovykh kislot)

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 4, pp 690-694 (USSR)

ABSTRACT: In the present work it has been confirmed that various α,α-diamino acids can easily be obtained in the form of derivatives by the method recently proposed (Refs 20-23). This has made the production of many of these acids possible. It has been found that a quick reaction of the aniline used in the reaction (aniline, benzylamine, piperidine) with the oxazolinone ring makes it possible for this amine to act directly on the intermediate product, bromooxazolinine (III). This gives the corresponding amides of α-amino-α-acylamino-carboxylic acids of type (IV) in a good yield (Schemes (I) → (II) → (III) → (IV) and Tables 1 and 2).

Card 1/3

If the amine used opens the oxazolinone ring only slowly, secondary reactions (polymerization, resinification) are observed, whereby the yield of the final compound is reduced. In some cases (IV) cannot be precipitated at all in individual form (Table 1). In these cases the oxazolinone ring must be opened first by another reagent. The corresponding esters of α-amino-α-acylaminocarboxylic acids (VI) can be synthesized in a satisfactory yield if 1 mole of any alcohol (or mercaptan) is previously caused to act on bromooxazolinone (III). These compounds may also be synthesized with such amines (aniline, benzylamine, piperidine, etc) as are suitable for the synthesis of amides of type (IV). (Schemes (I) → (II) → (III) → (V) → (VI) and Table 2). It must be mentioned that this reaction is accompanied by secondary conversions in some cases. Another synthesis of the substituted α,α-diamino-carboxylic acids has been found durin an investigation of the properties of α-hydroxy-α-acylamino acids (VIII). It has been found that these acids can be converted into α,α-di-(acyl-amino) acids (IX) when heated with acid amides. Some of these

Investigations in the Field of the [illegible] SOV/62-59-4-[illegible]
α-Amino Acids. Communication 5. Methods of Preparing Substituted
α,α-Diaminocarboxylic Acids

acids have been syrthesized by this method (Table 2). There are 2 tables and 26 references, 8 of which are Soviet.

ASSOCIATION: Institut biologicheskoy i meditsinskoy khimii Akademii meditsinskikh nauk SSSR (Institute of Biological and Medical Chemistry of the Academy of Medical Sciences, USSR), Moskovskiy tekstil'nyy institut (Moscow Textile Institute)

SUBMITTED: July 13, 1957

Card 3/3

5(3)

AUTHORS: Shemyakin, M. M., Shigorin, D. N., Shchukina, L. A., Semkin, Ye. P.

SOV/62-59-4-20/42

TITLE: Structure and Mechanism of the Hydrolytic Splitting of α-Nitro-α-Phenylacetophenon o-Carboxylic Acid (Stroyeniye i mekhanizm gidroliticheskogo rasshchepleniya α-nitro-α-fenil-atsetofenon-o-karbonovoy kisloty)

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 4, pp 695-698 (USSR)

ABSTRACT: To determine the structure of α-nitro-α-phenylacetophenone-o-carboxylic acid and its salts the spectra of these compounds were investigated in the present work (Table 1). These investigations have provided an answer to the question relating to their structure and their different behavior in the presence of hydrolyzing agents. As was to be expected, α-nitro-α-phenylacetophenone-o-carboxylic acid, like other aromatic o-aldehyde-(keto)-acids, has the structure of lactol (IIIb) rather than that of the keto acid (IV) in the crystalline state as well as in solution. After the actual structure of the α-nitro-α-phenylacetophenonic acid and of its disodium salt had been clarified, its different behavior in the

Structure and Mechanism of the Hydrolytic Splitting of SOV/62-59-4-20/42
α-Nitro-α-Phenylacetophenon -o-Carboxylic Acid

presence of hydrolyzing agents has been understood. As was shown before (Ref 3) the C—C bonds can split in those compounds in which a prototropic group (V) is present or can be formed in the molecule. The tendency to split depends directly on the degree of polarization of the C—C bond under the action of the substituent. α-Nitro-dinitrophenylacetophenone-o-carboxylic acid itself, having a lactol (IIIb) structure, does not only contain the required group (V) but also a nitro group which can polarize the splitting bond to a very high degree in the required direction. For this very reason the acid (IIIb) splits easily to form phthalic acid anhydride and phenylnitromethane if the pH-value of the solution exceeds 7. In the molecule of the disodium salt, on the other hand, the prototropic group (V) is not contained nor can it be formed by hydration owing to the structure of this salt. This fact is responsible for the resistance of this compound to hydrolytic splitting. There are 1 table and 11 references, 8 of which are Soviet.

Card 2/3

Structure and Mechanism of the Hydrolytic Splitting of α-Nitro-α-phenylacetophenon -o-Carboxylic Acid

SOV/62-59-4-20/42

ASSOCIATION: Institut biologicheskoy i meditsinskoy khimii Akademii meditsinskikh nauk SSSR (Institute of Biological and Medical Chemistry of the Academy of Medical Sciences, USSR)

SUBMITTED: July 13, 1957

Card 3/3

5(3) SOV/20-128-1-30/58

AUTHORS: Shemyakin, M. M., Academician, Kolosov, M. N., Arbuzov, Yu. A., Hsieh Hu-yüan, Sheng Huai-yü, Sklobovskiy, K. A., Karapetyan, M. G., Gurevich, A. I.

TITLE: Intermediate Stages in the Synthesis of Tetracyclines

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 128, Nr 1, pp 113-116 (USSR)

Received 4 June 1958

ABSTRACT: In 1956 the authors synthesized tricyclic ketols of kind (I) (Ref 1). They are similar to tetracyclines (III) as far as the structure of two rings is concerned. In the third ring they have a reactive double linkage in position 2,3. The present paper investigates the addition of heterogeneous reagents to the 2,3-double linkage of compounds (I) for introducing active groups into their molecules. The active groups are necessary for establishing a γ-grouping (II) in the B-ring and for a further extension of the A-ring of tetracyclines by a method previously elaborated. Investigations have shown that compounds (I) with typical electrophilic reagents such as Hal_2, RCO_3H and HOHal react readily. Thus, corresponding

Card 1/2 halogen derivatives, epoxides, hydrine halides, and halogen

Intermediate Stages in the Synthesis of Tetracyclines

ketones with good yields are formed. Constants and analytical results of synthesized compounds are given in table 1. The synthesis of tricyclic ketols with active groups in the B-ring made by the authors provides the possibility of building up the A-ring of tetracyclines. There are 1 table and 3 references, 2 of which are Soviet.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo AN SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy, AS USSR).
Institut biologicheskoy i meditsinskoy khimii AMN SSSR (Institute of Biological and Medical Chemistry, AMN USSR)

SUBMITTED: June 4, 1958

(3)

AUTHORS: Shemyakin, M. M., Lur'ye, M. Yu. SOV/79-29-8-15/81

TITLE: Investigations of the Chemistry of Chloromycetin (1 Mycetin). IX. Synthesis of the New Analog of Chloromycetin (D-TREO-1-(n-formylphenyl)-2-dichloroacetylamino-1,3-propanediol)

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 8, pp 2531 - 2533 (USSR)

Submitted 11 July 1958

ABSTRACT: Of the analogs of chloromycetin (I, R=$CHCl_2$) this hitherto undescribed analog is of special importance (IV, X=CHO; R=$CHCl_2$). The presence of the aldehyde group within it allows for the synthesis of a large number of other hitherto little accessible chloromycetin analogs, which are important for the further explanation of the varied dependence of the antimicrobic activity on the structure of these compounds. On the basis of the method elaborated by W. F. Beech (Ref 2) for the introduction of the aldehyde group into the aromatic ring by way of diazo compounds, the authors succeeded in applying the simple synthesis of optically active chloromycetin analogs (IV, R=$CHCl_2$) directly from chloromycetin (I, R=$CHCl_2$), suggested by them (Ref 3), for the

Card 1/3

Investigations of the Chemistry of Chloromycetin (1-Mycetin). IX. Synthesis of the New Analog of Chloromycetin (D-TREO-1-(n-formylphenyl)-2-dichloroacetylamino-1,3-propanediol) SOV/79-29-8-15/81

synthesis of the aldehyde they were interested in (Schemes). Initially, the transformation did not proceed from compound (I) but from its racemic N-benzyl analog (I, R=C_6H_5), since in this way crystallizing compounds are more easily obtained. With it, the diazo group was replaced by the aldehyde group in compound (III, R=C_6H_5) under conditions suggested by Beech (Ref 2) as an optimum. Compound (IV, X=CHO; R=C_6H_5) was easily separated in crystalline form (yield 15%). This aldehyde was then characterized in the form of the 2,4-dinitrophenyl hydrazone and other derivatives. The synthesis of compound (IV, X=CHO; R=$CHCl_2$) proceeded more difficultly. It was synthesized as above from compound (III, R=$CHCl_2$). However, it was not possible to obtain it in crystalline state even after careful purification. This aldehyde was characterized in the form of the 2,4-dinitrophenyl hydrazone (yield 12%). There are 3 references, 2 of which are Soviet.

Card 2/3

Investigations of the Chemistry of Chloromycetin (Levomycetin). IX. Synthesis of the New Analog of Chloromycetin (D-TREO-1-(n-formylphenyl)-2-dichloroacetylamino-1,3-propanediol) SOV/79-29-8-15/81

ASSOCIATION: Institut biologicheskoy i meditsinskoy khimii Akademii meditsinskikh nauk SSSR (Institute of Biological and Medical Chemistry of the Academy of Medical Sciences, USSR)

SUBMITTED: July 11, 1958

Card 3/3

B-3-30,B-3-40,B-3-10

SOV/79-29-12-21/43

AUTHORS: Shemyakin, M. M., Ravdel', G. A., Chaman, E. S., Shvetsov, Yu. B., Vinogradova, E. I., Vdovina, R. G., Yermolayev, K. M., Bamdas, E. M.

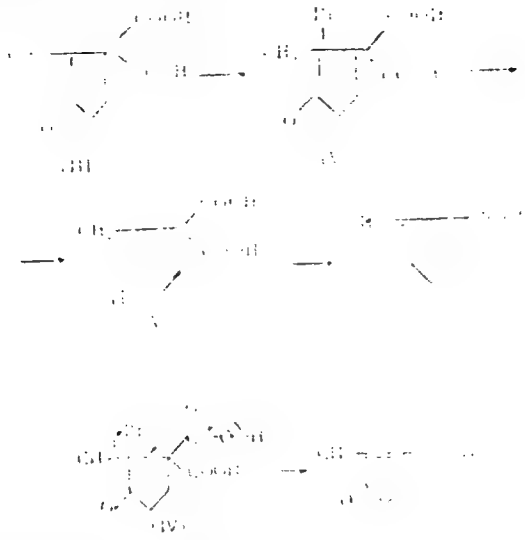
TITLE: Studies in the Field of Sarcomycine and Its Analogs. Communication 4. Study of Synthetic Routes to Sarcomycine and Its Analogs

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 12, pp 2177-2187 (USSR)

ABSTRACT: 2-Methylcyclopentan-3-one-1,1-dicarboxylic acid (III) was used for the preparation of (Sarcomycine) 2-methyl-one-cyclopentanone-3-carboxylic acid (I). (III) was assumed to be converted into (V) by bromination. It seemed possible to synthesize (I) from (V) by removal of HBr and by decarboxylation. Diacid (V) could not be obtained because elimination of HBr from (IV) and simultaneous decarboxylation formed (VI) with an endocyclic double bond.

Card 1/10

Studies in the Field of Sarcomycins and Its Analogs. Communication 4. Study of Synthetic Routes to Sarcomycins and Its Analogs

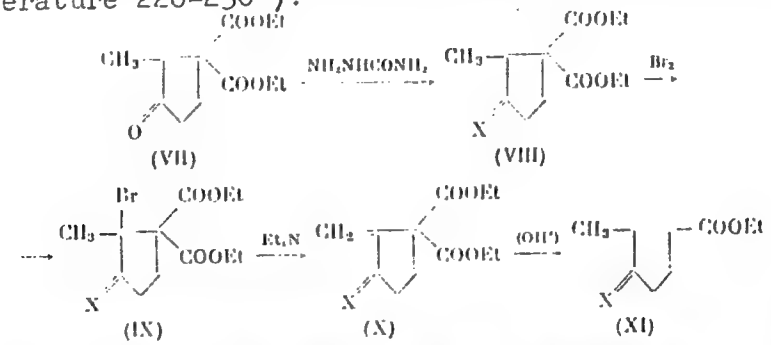


Card 2/10

Studies in the Field of Sarcomycine and Its Analogs. Communication 4. Study of Synthetic Routes to Sarcomycine and Its Analogs

77077
SOV/62-59-12-21/43

The semicarbazone of the diethyl ester of 2-methylcyclopentan-3-one-1,1-dicarboxylic acid (VIII) was brominated, and after eliminating HBr the semicarbazone of the diethyl ester of 2-methylenecyclopentan-3-one-1,1-dicarboxylic acid (X) was obtained in 56% yield (mp 207-209°). Diester (X) was saponified and the semicarbazone of the ethyl ester of 2-methylcyclopenten-1-one-3-carboxylic acid (XI) was obtained, in 74% yield (dec. temperature 220-230°).



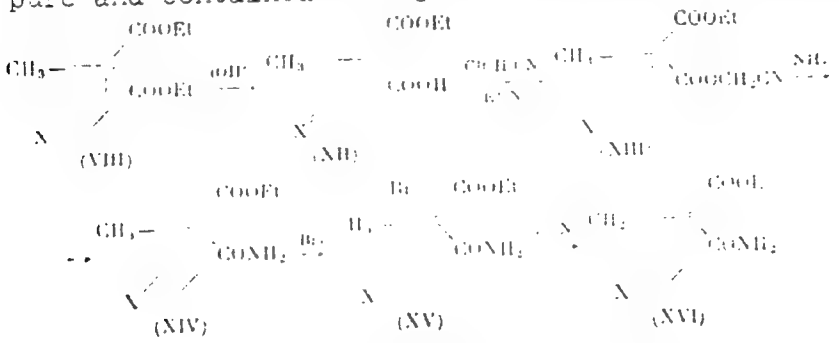
where X = $NNHCONH_2$.

Card 3/10

Studies in the Field of Sarcomycine and Its Analogs. Communication 4. Study of Synthetic Routes to Sarcomycine and Its Analogs

77077
SOV/62-59-12-21/43

Attempts were made to convert the semicarbazone of the amide of 1-carbethoxy-2-methylcyclopentanene-3-carboxylic acid (XIV) into the semicarbazone of the amide of 1-carbethoxy-2-methylenecyclopentanone-3-carboxylic acid (XVI), but the isolated compound (XVI) was not pure and contained from 30 to 40% polymeric material.

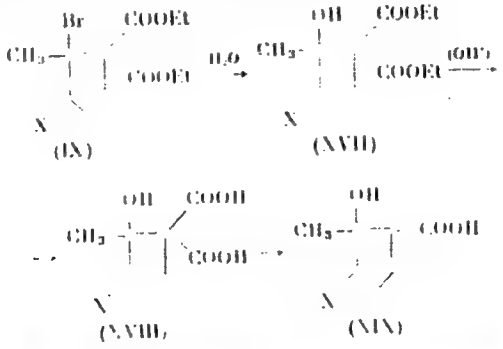


Card 4/10

Studies in the Field of Sarcomycine and Its Analogs. Communication 4. Study of Synthetic Routes to Sarcomycine and Its Analogs

77077
SOV/62-59-12-21/43

Semicarbazone of the diethyl ester of 2-methylcyclopentan-2-olone-3-carboxylic acid (XVII) was obtained, in 81% yield (mp 160-161°), from (IX) by reaction with water. Semicarbazone of 2-methylcyclopentan-2-olone-3-carboxylic acid (XIX) was prepared in 38% yield (mp 187-188°) by saponification of (XVII) and by subsequent decarboxylation of the intermediate (XVIII).



Card 5/10

Studies in the Field of Sarcomycine and Its Analogs. Communication 4. Study of Synthetic Routes to Sarcomycine and Its Analogs

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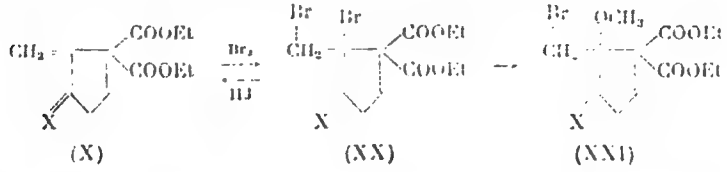
SOV/62-59-12-21/43

Dibromide (XX) was obtained quantitatively (mp 82-85° dec.) by addition of two bromine atoms to the diester (X). In the compound (XX) one bromine atom (position 2) is very labile. (XX) reacts with CH_3OH or H_2O forming corresponding compounds (XXI) in 65% yield (mp 138-139°) or (XXII) in 83% yield (mp 148-149°). The labile bromine atom in compound (XX) can quantitatively oxidize KI to free iodine, in the cold, but the obtained product can not be isolated, because the reaction is accompanied by elimination of HBr and formation of diester (X) in 71% yield (mp 207° dec.).



(X) (XX) (XXI)

Card 6/10

Studies in the Field of Sarcomycine and Its Analogs. Communication 4. Study of Synthetic Routes to Sarcomycine and Its Analogs

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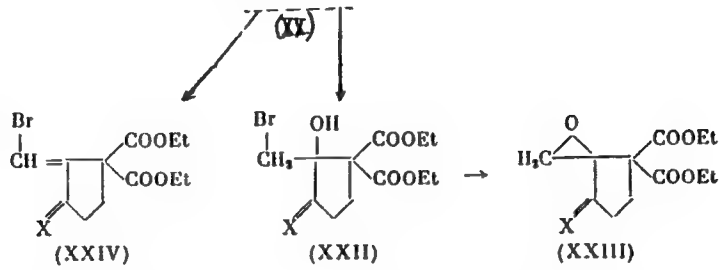
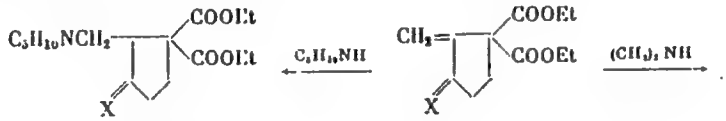
SOV/62-59-12-21/43



where $X = NNHCONH_2$.

Compound (X) was converted into corresponding amines (XXV), in 17% yield (mp 124-126°), and (XXVI), in 62% yield (m p 160-161°), according to the reaction:



Card 7/10

Studies in the Field of Sarcomycine and Its Analogs. Communication 4. Study of Synthetic Routes to Sarcomycine and Its Analogs

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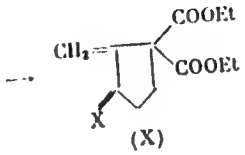

(X)

where X = $NNHCONH_2$.

The synthesis of (I) may take place as follows: amines of (XXV-XXVI)-type, after hydrolysis, decarboxylation, and formation of the methylene group, can be converted into (I). The results of investigation will be published in a forthcoming communication. There are 9 references, 3 Soviet, 1 German, 2 Japanese, 1 U.K., 2 U.S. The 3 U.S. and U.K. references are: Chem. and Industr. 1957, 1320; E. J. Corey, J. Amer. Chem. Soc. 75, 1163 (1953); J. R. Hooper, L. C. Cheney et al., Antibiot. and Chemother. 5, 585 (1955).

Card 9/10

Studies in the Field of Sarcomycine and Its Analogs. Communication 4. Study of Synthetic Routes to Sarcomycine and Its Analogs

77077
SOV/62-59-12-21/43

ASSOCIATION: Institute of Biological and Medical Chemistry, Academy of Medical Sciences (Institut biologicheskiy i meditsinskoy khimii Akademii medicinskhikh nauk)

SUBMITTED: April 12, 1958; Additions made, December 28, 1958

Card 10/10

Investigation in the Field of Sarcomycine and Its Analogs. Communication 5. Synthesis of Racemic Sarcomycine

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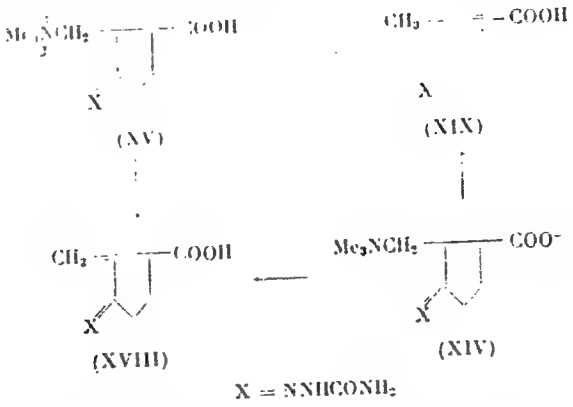
SOV/62-59-12-22/43



The ethyl ester of 2-dimethylaminomethylcyclopentanone-3-carboxylic acid (XI) was used as starting material for the preparation of (III). Racemic sarcomycine in the form of its semicarbazone (XVII) can be obtained, in 39% yield, from the methiodide of acid (XV) or from betaine (XIV) together with the semicarbazone of 2-methylcyclopenten-1-one-3-carboxylic acid (XIX). For

Card 2/4

this purpose (XV) or (XIV) is heated on a water bath for 4 minutes with 2 moles (for betaine 1 mole) of 1N NaOH. The solution was cooled to 0-2°, 10% HCl was added, and after 30 minutes the precipitate was removed by filtration and washed with cold water. The mixture of (XVIII) and (XIX) was obtained in 39% yield. The compound turns black on heating, but does not melt. Found: C 48.87%; H 6.02%. $C_8H_{11}O_3N_3$. Calculated: 48.75%; H 5.63%. From the above mixture, the semicarbazone of racemic sarcomycine (XVIII) was isolated by crystallization, in 50-55% yield. There are 8 references, 3 Soviet, 1 Japanese, 1 U.K., 3 U.S. The 4 U.S. and U.K. references are: Chem. and Industr. 1957, 1320. G. Buchi, N. G. Yang and Others, Chem. and Industr. 1953, 1063; J. Meinwald, S. L. Emerman and others., J. Amer. Chem. Soc. 77, 4401 (1955); E. E. Van Tamelen, S. R. Bach, J. Amer. Chem. Soc. 77, 4683 (1955).

Investigation in the Field of Sarcomycine and Its Analogs. Communication 5. Synthesis of Racemic Sarcomycine

77078
SOV/62-59-12-22/43

ASSOCIATION: Institute of Biological and Medical Chemistry, Academy of Medical Sciences (Institut biologicheskoy i meditsinskoy khimii Akademii meditsinskikh nauk)

SUBMITTED: April 12, 1958; Additions made, December 28, 1958

Card 4/4

5 (3) SOV/[illegible]-29-6-13/72

AUTHORS: Shemyakin, M. M., Kolosov, M. N., Arbuzov, Yu. A., Karapetyan, M. G., Chaman, Ye. S., Onishchenko, A. A.

TITLE: Investigations in the Field of Tetracyclines (Issledovaniya v oblasti tetratsiklinov). IV. Investigation of Different Syntheses of the Tricyclic System DCB of the Tetracyclines (IV. Izucheniye putey sinteza tritsiklicheskoy sistemy DCB tetratsiklinov)

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 6, pp 1831 - 1842 (USSR)

Received 7 June 58

ABSTRACT: The structure of the well-known tetracyclines (I) has a specific characteristic which indicates the ways and methods necessary for carrying out the complete synthesis of compounds of this type. On the basis of certain theoretical considerations the authors tried to synthesize such ketols of the hydroanthracene series of type (III) and (IV) in which two rings had to be similar with respect to structure and spatial arrangement to the rings D and C of the tetracyclines. The third ring had to offer the structural conditions for the subsequent building-up of the ring A and for the introduction of the necessary func-

Card 1/3

Investigations in the Field of Tetracyclines. IV. Investigation of Different Syntheses of the Tricyclic System DCB of the Tetracyclines

SOV/79-29-6-13/72

tional groups of the ring B of the tetracyclines. The adopted method of synthesizing these compounds consisted in the condensation of the 1,4-naphthoquinones with butadiene or its derivatives and the transformation of the resultant adducts (II) into the ketols (III) which, on their part, can easily be hydrolyzed to give the oxy-diketones (IV). The first step, the diene synthesis, takes place readily by heating naphthoquinone with the diene. By condensation of the 5-methoxy-naphtho-quinone with 2-methoxy-butadiene two isomeric adducts - (II d) and (II e) in the ratio 4 : 1 - are formed. The second step, the selective transformation of the C_9-keto group of the adducts (II) into the tertiary methyl carbinol grouping meets with some difficulties, it was however possible to carry out the reaction by means of magnesium methyl halide. The third step of the synthesis of the compounds (IV), the hydrolysis of the enol-methoxyl up to the keto group is only possible when using dilute acids. The synthesis of the tricyclines (XV) was thus performed on the basis of naphthoquinones, in which two rings are analogous with the rings D and C of the natural tet-

Card 2/3

Investigations in the Field of Tetracyclines. IV. Investigation of Different Syntheses of the Tricyclic System DCB of the Tetracyclines

SOV/79-29-6-13/72

racyclines with respect to structure and spatial arrangement. The presence of the reactive double bond, the enol grouping or the carbonyl group in the third ring of the compounds (XV) offers further possibilities for the introduction of substituents and for the building up of the fourth ring of the tetracyclines. There are 12 references, 4 of which are Soviet.

ASSOCIATION: Institut biologicheskoy i meditsinskoy khimii Akademii meditsinskikh nauk SSSR i Institut organicheskoy khimii Akademii nauk SSSR (Institute of Biological and Medical Chemistry of the Academy of Medical Sciences USSR, and Institute of Organic Chemistry of the Academy of Sciences, USSR)

SUBMITTED: June 9, 1958

Card 3/3

5(2, 3) SOV/20-128-3-36/58

AUTHORS: Shemyakin, M. M., Academician, Maymind, V. I., Yermolayev, K. M., Bamdas, E. M.

TITLE: On the Reaction Mechanism of Osazone Formation

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 128, Nr 3, pp 564-566(USSR)

ABSTRACT: In spite of many investigations (Refs 1-15), the formation of osazones from α-oxycarbonyl compounds remains unclear. All respective hypotheses and assumptions can be reduced to 3 schemes: A (Ref 1), B (Ref 3), and C (Ref 3). In order to find the correct scheme, the osazone reaction was marked with ^{15}N. If scheme A applies, the resulting ammonia may not contain an excess in ^{15}N, but the ^{15}N must completely remain in the osazone. If, however, scheme B is correct, the osazone will remain unmarked while the ammonia will contain the entire marking. Finally, if scheme C is the right one, the ^{15}N excess will be distributed, in equal shares, between osazone and ammonia. Unfortunately, the investigation of the mechanism under discussion by means of tagged atoms is much impeded by the fact that the marking may be diluted by exchange reactions, hydrolysis or substitution. These secondary processes could be avoided to a large extent, by producing the osazones in boiling isoamyl alcohol and removing the water from the reac-

Card 1/3

tion sphere. Then, the dilution of the marking in the hydrazone is inconsiderable at the beginning, and cannot conceal the reaction mechanism of osazone formation. Therefore, it can be rather accurately judged which of the 3 schemes really applies. For this purpose, the reaction must be interrupted after a certain period (depending on the type of hydrazone used). The investigations were carried out with β-^{15}N-p-nitrophenyl hydrazones of fructose, cyclohexanolone and benzoin. Boiling alcoholic solutions of the said hydrazone and of an unmarked p-nitrophenyl hydrazine (2 moles) were poured together, and subsequently boiled in the nitrogen current. The resulting ammonia was immediately removed from the reaction solution. The isolation and separation of osazone, hydrazone and hydrazine was done as quickly as possible under conditions which prevent a further change in the marking by exchange reactions. As they could not be fully eliminated, it was more convenient to measure the isotopic composition of ammonia, not of osazone. Table 1 shows that the escaping ammonia at first always contained much more than half of the marking of the initial hydrazone. Hence it is concluded that scheme B applies to all cases investigated. This scheme is distinguished from the others by the fact that the 1st reaction stage proceeds without par-

On the Reaction Mechanism of Osazone Formation SOV/20-128-3-36/58

ticipation of hydrazine. As was expected, it could be observed that the osazone-formation process can be divided into 2 stages with separation of an intermediate monoimine of α-diketone (I). By the example of p-nitrophenyl hydrazone of benzoin, it was ascertained that prolonged heating at 60° in glacial acetic acid and without hydrazine causes its disappearance. If 2 moles of hydrazine are subsequently added, an osazone precipitation is quickly formed. There are 1 table and 15 references.

ASSOCIATION: Institut biologicheskoy i meditsinskoy khimii Akademii meditsinskikh nauk SSSR
(Institute of Biological and Medical Chemistry of the Academy of Medical Sciences, USSR)

SUBMITTED: June 22, 1959

Card 3/3

these problems. A model synthesis and some transformations of the simplest compound of type (IVb) - the ester of threo-2-keto-cyclo-hexyl-N,N-dimethyl glycine (XIIa) - are described. The above-mentioned introduction into the cyclohexanone ring has to be carried out under such conditions and by such methods as are also applicable to the case of tricyclic oxydiketones (I). This method is described. The authors ascribed a threo-configuration to the dimethyl-amino-keto ester obtained. This was also confirmed by further transformations (XVIII) and (XIVa). Table 1 shows the compounds obtained, their constants, as well as the composition found analytically and by computation (VIa - XXII). The dimethyl-amino-keto ester (XIIa) synthesized by the authors was also investigated with respect to the introduction of an ethinyl residue into the molecule. This is necessary for building up the "lower" part of the A-ring of tetracyclines by the method developed previously (Ref 2). It was shown that (XIIa) easily reacts with $HC \equiv CNa$ in liquid NH_3 at -50° to form an acetylene-oxy ester in a 60% yield. The latter is supposed to

SOV/79-29-9-1/76

5(3)
AUTHORS: Semenov N. N., Shemyakin, M. M., Kochetkov, N. K.

TITLE: Academician Aleksandr Nikolayevich Nesmeyanov.(On His 60th Birthday)

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 9, pp 2811 - 2816 (USSR)

ABSTRACT: A. N. Nesmeyanov (born 9.9.1899 in Moscow) graduated from the Physical and Mathematical Department of Moscow University in 1922, became an assistant to the well-known chemist N. D. Zelinskiy, and later was appointed professor in ordinary and head of the Chair of Organic Chemistry; he attained the highest degree in 1947, when he was elected rector. He became a member of the Academy of Sciences in 1943, and of other institutions later on. An outstanding speaker, he has a special talent of rendering the most complicated subjects intelligible and pleasant. His activities have covered various fields, from a great number of problems belonging to elemental-organic chemistry to the synthesis of valuable new polymers, from theoretical problems of reaction mechanism and reactivity to the introduction of methods of synthesis relating to the compound

Card 1/3

SOV/79-29-9-1/76

Academician Aleksandr Nikolayevich Nesmeyanov.
(On His 60th Birthday)

heterocyclic systems. Among his numerous achievements the following deserve first mention: the simple method of synthesizing metal-organic compounds by the aid of aromatic diazocompounds, a method which is still regarded as the best for the synthesis of aromatic derivatives of mercury, antimony, arsenic. This method has been developed to apply to syntheses of aromatic compounds of tin, zinc, thallium, aluminum as well as organomercury-silver compounds from compounds of Sn, Pb, As, Sb, Cd, Tl, and others. Remarkable syntheses are the ones yielding iodonium-, bromonium-, and chloronium compounds, and finally, oxonium compounds by the arylation of bromo- and chlorobenzene, and of diphenyl ether with diazonium borofluoride. Great importance has been and still is attached to his investigations concerning the addition of metals to the unsaturated compounds of the olefin and acetylene series, the exchange of metal atoms in the compounds of the above metals containing a β-chlorovinyl radical. Nesmeyanov has developed a new conception of the manifold reactivity and displacement of the reaction center in the reactions of metal compounds. His attempt of solving

Card 2/3

Academician Aleksandr Nikolayevich Nesmeyanov. (On His 60th Birthday)

SOV/79-29-9-1/76

the problem of the mechanism of electrophilic substitution on the saturated carbon atom deserves special mention. He investigated the metallocenes, metal-organic compounds formed by the interaction of the s,p,d-electrons of the transition metals with the π-electrons of the unsaturated carbon bonds. The aromatic nature of ferrocene was proven by numerous reactions. From 1938 to 1954, Nesmeyanov was the head of the Institut organicheskoy khimii AN SSSR (Institute of Organic Chemistry AS USSR), from 1954 head of the Institut elementoorganicheskikh soyedineniy AN SSSR (Institute of Elemental-organic Compounds AS USSR); 1946-48, secretary of the Otdeleniye khimicheskikh nauk AN SSSR (Department of Chemical Sciences AS USSR), and since 1951 he is the President of the Akademiya nauk SSSR (Academy of Sciences, USSR). Since 1947 he is the chairman of the committee presiding over the scientific Lenin Prize awards (formerly called Stalin Prize). He was distinguished with the Lenin Order, the Order of the Red Workers' Banner, and the Stalin Prize First Class for scientific merits.

Card 3/3

[illegible]

AUTHORS: [illegible] Arbuzov, Yu., [illegible], M. N., [illegible], V. A., [illegible], V. V., [illegible], M. I.

TITLE: [illegible] VI. [illegible] of Dienes With Long [illegible]

PERIODICAL: [illegible] (USSR)

ABSTRACT: [illegible] Condensation of dimedone with [illegible] derivatives [illegible] one of the following [illegible]. There are [illegible] references, [illegible] Soviet, [illegible] German, 1 U.S. The U.S. reference is: R. L. Frank, H. K. Hall, J. Am. Chem. Soc., 72, [illegible] ([illegible]).

ASSOCIATION: Institute of Organic Chemistry, Academy of Sciences, USSR (Institut organicheskoy khimii Akademii nauk SSSR)

SUBMITTED: [illegible]

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77886
SOV/79-30-2-37/78

AUTHORS: Shemyakin, M. M., Kolosov, M. N., Arbuzov, Yu. A., Onoprienko, V. V., Sieh Yü-yüan

TITLE: Investigation in the Field of Tetracyclines. VII. Study of the Synthetic Routs to the A Ring of Tetracyclines

PERIODICAL: Zhurnal obshchey khimii, 1960, Vol 30, Nr 2, pp 545-556 (USSR)

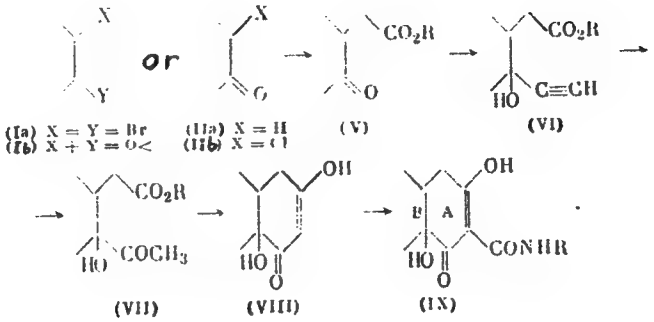
Submitted 25 Feb 1959

ABSTRACT: Synthesis of compound IX can be divided into three parts: (1) construction of the upper parts of the A ring (Ia (Ib) or IIa (IIb) → (V)); (2) construction of its lower parts (V→VI→VII); and cyclization with subsequent introduction of carboxamide group (VII→ VIII→IX).

Card 1/11

Investigation in the Field of Tetracyclines. VII. Study of the Synthetic Routs to the A Ring of Tetracyclines

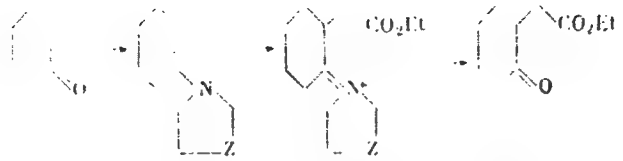
77886
307/79-30-2-37/78



The following compounds can be used for construction of the upper ring: dibromides (Ia); epoxides (Ib); ketones (IIa); and haloketones (IIb). The third way (IIa) is simpler.

Card 2/11

Investigation [illegible] VII. Study of the Synth[illegible] Ring of Tetracyclines



(X) (XI) (XII)

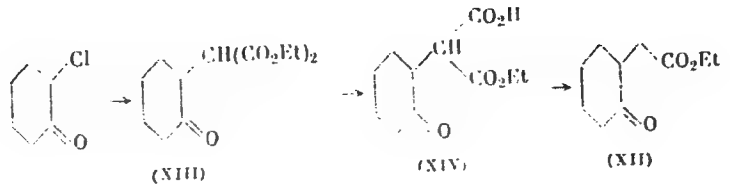
Z = CH_3, $(CH_2)_x$ or OCH_3.

The fourth way (IIb) puts the carbomethoxy group exclusively in a certain position of cyclohexane ring.

Card 3/ 11

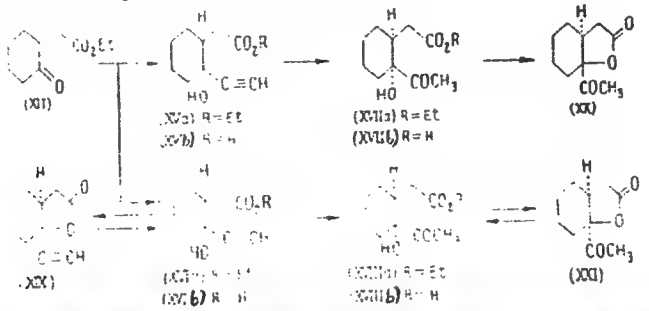
Investigation in the Field of Tetracyclines. VII. Study of the Synthetic Route to the A Ring of Tetracyclines

77[illegible]
SOV/79-30-2-37,7c



(XIII) (XIV) (XII)

Construction of lower parts of the A ring includes ethynylation of V and hydration of the triple bond of the obtained ethynyl carbinol (VI).

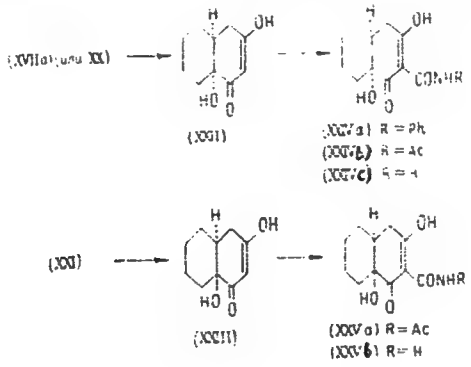


Card 4/11

Investigation in the Field of Tetracyclines. VII. Study of the Synthetic Route to the A Ring of Tetracyclines

[illegible]
[illegible]

Na-enolates of hydroxydiketones react in dimethylformamide with excess of the corresponding isocyanate (carboxyamidation of hydroxydiketones XXII and XXIII).



Card 5/ 11

Investigation in the Field of Tetracycl[illegible]. 77886
VII. Study of the Synthetic Route to the A SOV/79-30-2-37/78
Ring of Tetracyclines

Some Properties of Obtained Products

Nr	Starting Material	Obtained Product	Yield (%)	mp, mm pr	$n_D^{(x)}$
1	Cyclohexanone + secondary amine* tolunesulfonic acid + benzene	X	-	-	-
2	X + bromoacetic ester + hydrolysis with aqueous methanol	XII	-	121-122°/7	x = 18 1.4592
3	Sodium malonic ester + 2-chlorocyclohexanone + malonic ester + benzene	XIII	70	151-153°/3	x = 20 1.4595

* piperidine, pyrrolidine, morpholine.

Card 6/11

Investigation in the Field of Tetracyclines. VII

77880
SOV/79-30-2-37/78

Nr	Starting Material	Obtained Product	Yield (%)	bp/mm pr	$n_D^{(x)}$
4	Saturated HC≡CH solution in liquid ammonia + Na + XII + abs. ether + NH_4Cl	mixture of XV-a and XVI-a	85	83-84°/0.02	x = 18 1.4831
5	Mixture of XVa and XVI-a are hydrolyzed with NaOH	XV-b + mother liquid	71	mp 101-2°	-
6	the above mother liquid (5) + 0.1N H_2SO_4	XIX	24	63-64°/0.04	x = 21 1.4926
7	XIX is hydrolyzed with 0.1 N NaOH, acidified with 1 N H_2SO_4, and extracted with $CHCl_3$	XVI-b	-	-	-

Card 7/11

Investigation in the Field of Tetracyclines. VII

77886
SOV/79-30-2-37/78

Nr	Starting Material	Obtained Product	Yield (%)	bp/mm pr	n_D (x)
8	Mixture of XVa and XVIa + anhydrous alcohol + mercuric acetate	mixture of XVII-a and XVIII-a	66	90-92°/0.03	x = 17 1.4735
9	Mixture of XVa and XVIa + mercuric salt of p-toluenesulfonamide + alcohol	mixture of XVII-a and XVIII-a	41	-	-
10	Mixture of XVIIa and XVIIIa + alcohol + hydrolysis with 0.4 N NaOH	XVII-b + mother liquid	72	mp 115-6°	-
11	The above mother liquid (10) is boiled with 1 N H_2SO_4	XXI	24	72-73°, 0.03	-

Card 8/11

Investigation in the Field of Tetracyclines. VII

77886
SOV/79-30-2-37/78

Nr	Starting Material	Obtained Product	Yield (%)	bp/mm pr	$n_D^{(x)}$
12	XXI is hydrolyzed with 0.1 N NaOH	XVIII-b	96	mp 98-100°	-
13	XVII-b is heated at 150°/15 mm	XX	91	70-71°/0.12	x = 22 1.4828
14	XVIII-c + Na_2CO_3 + $AgNO_3$ + ethyl iodide	XVII-a	90	91-92°/0.03	x = 19 1.4737
15	XVII-b or XVIII-b is distilled at 130°/0.07	XVIII-b trans in the form of lactone	88	-	-

Card 9/11

Investigation in the Field of Tetracyclines. VII

77886
SOV/79-30-2-37/78

Nr	Starting Material	Obtained Product	Yield (%)	bp/mm pr	n_D (x)
16	XVII-b or XXVIII-b + 0.1 N H_2SO_4 after 2 hours	XVIII-b in the form of lactone	100	-	-
17	XVII-a + 0.5 N sodium ethoxide in alcohol	XXII (cis)	95	mp 181-182°	-
18	XXII (cis) + dimethylformamide + phenylisocyanate	XXIV-a	46	-	-
19	XXIV-b + NH_3 + CH_3OH	XXIV-b (cis)	75	mp 153-154°	-
20	XXV-a + ammonolyse	XXV-b (trans)	65	mp 160-161°	-

Card 10/11

SHEMYAKIN, Mikhail M.

"Synthesis of Depsipeptides."

report to be submitted for the Symposium on the Chemistry of Natural Products, Intl. Union of Pure and Applied Chem.(IUPAC), Melbourne, Canberra, and Sydney, Australia, 15-25 August 1960

Prof. Act. Mbr., Acad. Sci. USSR
Dir. Inst. of the Chemistry of Natural Compounds, Moscow

SHEMYAKIN, M.M.; MAYMIND, V.I.; VAYCHUNAYTE, B.K.

Studies of compounds tagged with C^{14} and N^{15}. Report No.10: Reaction involving the isomerization of azoxy compounds, as studied with the use of N^{15}. Izv.AN SSSR Otd.khim.nauk no.5: 866-871 My '60. (MIRA 13:6)

1. Institut biologicheskoy i meditsinskoy khimii Akademii meditsinskikh nauk.
(Azoxy compounds) (Nitrogen--Isotopes)

BERGEL'SON, L.D.; MOLOTKOVSKIY, Yu.G.; SHEMYAKIN, M.M.

Synthesis of macrocyclic diacetylenic lactones. Izv.AN SSSR. Otd.khim.nauk no.6:1139 Je '60. (MIRA 13:7)

1. Institut khimii prirodnykh soyedineniy Akademii nauk SSSR.
(Lactones) (Acetylene compounds)

BERGEL'SON, L.D.; VAVER, V.A.; SHEMYAKIN, M.M.

New method of synthesizing unsaturated acids. Izv. AN SSSR Otd. khim. nauk no.10:1900 O '60. (MIRA 13:10)

1. Institut khimii prirodnykh soyedineniy AN SSSR.
(Unsaturated compounds) (Acids, Organic)

SHEMYAKIN, M.M., akademik; ARBUZOV, Yu.A.; KOLOSOV, M.N.; OVCHINNIKOV, Yu.A.

Study of the synthetic paths used in building the ring system of BA tetracyclines. Dokl.AN SSSR 133 no.5:1121-1124 Ag '60. (MIRA 13:8)

1. Institut khimii prirodnykh soyedineniy Akademii nauk SSSR i Moskovskiy gosudarstvennyy universitet im. M.V.Lomonosova.
(Tetracycline)

SHEMYAKIN, M.M., akademik; AGADZHANYAN, TS.Ye.; MAYANTS, V.I.; KUDRYAVTSEV, R.V.; KURSANOV, D.N.

Study of the isomerizations of azoxy compounds by means of O^{18}. Dokl. AN SSSR 135 no.2:346-349 N '60. (MIRA 13:11)

1. Institut biologicheskoy i meditsinskoy khimii AMN SSSR i Institut elementoorganicheskikh soyedineniy AN SSSR. 2. Chlen-korrespondent AN SSSR (for Kursanov).
(Oxygen--Isotopes) (Azoxy compounds)

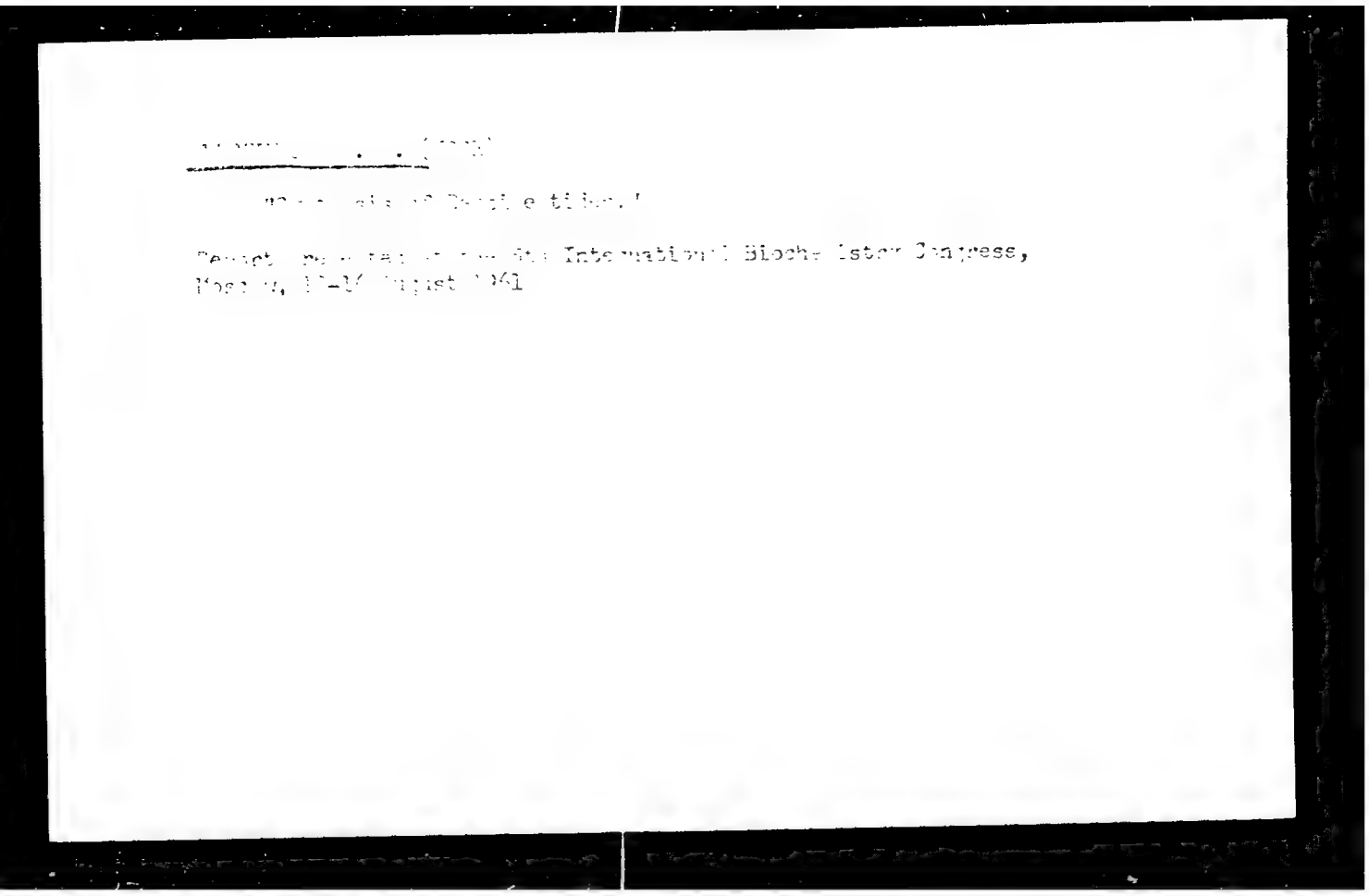
SHEMYAKIN, Mikhail Mikhaylovich; KHOKHLOV, Aleksandr Stepanovich; KOLOSOV, Mikhail Nikolayevich; BERCEL'SON, Lev Davydovich; ANTONOV, Vladimir Konstantinovich; SHVETSOV, Yu.B., red. izd-va; DOROKHINA, I.N., tekhn. red.

[Chemistry of antibiotics] Khimiia antibiotikov. Izd.3., perer. i dop. Moskva, Izd-vo Akad. nauk SSSR. Vol.1. 1961. pp.1-774. Vol.2. 1961. pp. 780-1550. (MIRA 14:8)
(ANTIBIOTICS)

SHEMYAKIN, M. M. (USSR Acad. Sci. Moscow)

"The Chemistry of Depsipeptides."

report submitted for the International Chemistry Symposium, Stanford University, 1-3 March 1961



SHEMYAKIN, M. M., BERGELSON, L. D., YAVER, M. M. (USSR).

"A New Way of Fatty Acid Synthesis."

Report presented at the 5th International Biochemistry Congress, Moscow, 10-16 August 1961

BERGEL'SON, L.D.; DYATLOVITSKAYA, Ye.V.; SHEMYAKIN, M.M.

Intramolecular trans-acetalization accompanied by the formation of 1,3-dioxanes. Izv. AN SSSR. Otd. khim. nauk no.2:358-359 F '62. (MIRA 14:2)

1. Institut khimii prirodnykh soyedineniy AN SSSR.
(Dioxane) (Acetals)

ARBUZOV, Yu.A.; KOLOSOV, M.N.; OVCHINNIKOV, Yu.A.; SHEMYAKIN, M.M.

New reaction of halo lactones. Izv. AN SSSR, Otd. khim. nauk no.2: 377 F '61. (MIRA 14:2)

1. Institut khimii prirodnykh soyedineniy AN SSSR.
(Lactones)

BERGEL'SON, L.D.; VAVER, V.A.; SHEMYAKIN, M.M.

Effect of the solvent on the steric course of the Wittig reaction.
Izv.AN SSSR Otd.khim.nauk no.4:729-730 Ap '61. (MIRA 14:4)

1. Institut khimii prirodnykh soyedineniy AN SSSR.
(Chemical reaction)